

# Carboxylation of benzene with CO and O<sub>2</sub> catalyzed by Pd(OAc)<sub>2</sub> combined with molybdovanadophosphates

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Received 24 July 2007; received in revised form 19 November 2007; accepted 23 November 2007

Available online 9 January 2008

## Abstract

Carboxylation of benzenes with CO was successfully achieved by a combined catalytic system of Pd(OAc)<sub>2</sub> with H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·nH<sub>2</sub>O (HPMo<sub>10</sub>V<sub>2</sub>) under the influence of O<sub>2</sub> to form the corresponding benzoic acids in relatively high selectivity and moderate yields. The regioselectivity in the carboxylation of alkylbenzenes with CO was dominated by the steric factor rather than the electronic effect of substituents. However, the carboxylation of benzoic acid proceeded with high *ortho*-selectivity to give phthalic acid in preference to terephthalic acid, which shows coordination of Pd species to the carboxyl group of benzoic acid.

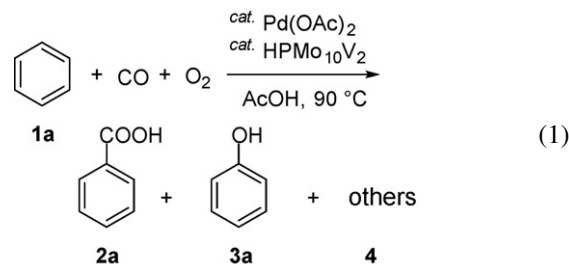
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**Keywords:** Molybdovanadophosphoric acids; Carboxylation; Benzene

## 1. Introduction

A stoichiometric direct carboxylation of benzene with CO was first reported by Fujiwara et al. by the use of Pd(OAc)<sub>2</sub> [1]. Thereafter, they reported the Pd-catalyzed carboxylation of benzene derivatives with CO using *t*-BuOOH [2] or K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> [3] as reoxidants in trifluoroacetic acid. Recently, they have reviewed the Pd(II)-catalyzed carboxylation of hydrocarbons with CO [4]. On the other hand, Nozaki et al. reported the Pd(OCOFCF<sub>3</sub>)<sub>2</sub>-catalyzed carboxylation of benzene with formic acid and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in a mixed solvent of CF<sub>3</sub>COOH and (CF<sub>3</sub>CO)<sub>2</sub>O [5]. Alternatively, the Pd(II)-catalyzed carboxylation of arenes like benzene with CO and O<sub>2</sub> directly gives benzoic acid derivatives, but it is still difficult to carry out despite their importance. Difficulty in achieving the carboxylation using CO and O<sub>2</sub> is believed to be due to the fact that the PdCl<sub>2</sub>/CuCl<sub>2</sub>/O<sub>2</sub> system often promotes not only the carboxylation but also the oxidation of CO to CO<sub>2</sub>. We have recently found that molybdovanadophosphoric acids (HPMoV) serve as an efficient reoxidation catalyst of the reduced Pd(0) to Pd(II) using O<sub>2</sub> which acts as a terminal oxidant. Thus, the carbomethoxylation of alkenes with CO and O<sub>2</sub> was achieved by Pd(OAc)<sub>2</sub> using

HPMoV as the reoxidation catalyst of the reduced Pd(0) [6]. We have found that Pd(OAc)<sub>2</sub> combined with HPMoV is an efficient catalytic system for the direct activation of the C–H bond of arenes using molecular oxygen as the reoxidant. Thus, the Heck–Mizoroki reaction of benzene with acrylate was first achieved by using the Pd(OAc)<sub>2</sub>/HPMoV/O<sub>2</sub> system [7]. By the use of this catalytic system, the carboxylation of anisole derivatives and biphenyl under a mixed gas of CO and O<sub>2</sub> gave the corresponding anisic acids and biphenyl carboxylic acid, respectively, in fair to good yields [8,9], but the carboxylation of benzene was difficult, giving benzoic acid in poor yield. We have now found that the catalytic activity for the carboxylation of benzenes with CO by the Pd(OAc)<sub>2</sub>/HPMoV/O<sub>2</sub> system is markedly dependent on the preparation method of HPMoV. In this paper, we would like to report the direct carboxylation of benzene (**1a**) to benzoic acid (**2a**) with CO and O<sub>2</sub> by Pd(OAc)<sub>2</sub> combined with HPMoV (Eq. (1)).



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Table 1  
Carboxylation of benzene (**1a**) to benzoic acid (**2a**) with CO and O<sub>2</sub> by Pd(II) combined with HPMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·*n*H<sub>2</sub>O prepared by various methods<sup>a</sup>

Entry	Preparation method of H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> · <i>n</i> H <sub>2</sub> O <sup>b</sup>	Conversion (%)	Yield (%)		
			<b>2a</b> <sup>c</sup>	<b>3a</b>	Others
1	A	50	26	0	24
2 <sup>d</sup>	A	90	42 <sup>e</sup> (34) <sup>f</sup>	0	48
3	B	6.7	0.6	2.9	3.2
4	C	8.8	Trace	2.0	6.8
5	D	36	16	Trace	20
6	E	5.2	0.5	0.8	3.9

<sup>a</sup> **1a** (2 mmol) was reacted in AcOH (5 mL) under CO (0.5 atm) and O<sub>2</sub> (0.5 atm) by Pd(OAc)<sub>2</sub> (0.1 mmol) and H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> (0.04 mmol) at 90 °C for 15 h.

<sup>b</sup> A: H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·26H<sub>2</sub>O prepared by Grate method. B: H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·15H<sub>2</sub>O prepared by Hallada method. C: H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·22H<sub>2</sub>O by Hallada method.

D: A part of H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·27H<sub>2</sub>O (1.7 g) obtained by recrystallization from aqueous solution of B (2.5 g). E: A part of H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·22H<sub>2</sub>O obtained from filtrate of D.

<sup>c</sup> The yields after esterification with ethanol.

<sup>d</sup> For 60 h.

<sup>e</sup> Phthalic acid (2.5%) was formed.

<sup>f</sup> Isolated yield as ethyl benzoate.

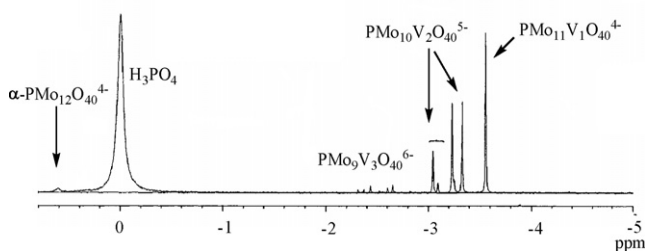


Fig. 1. <sup>31</sup>P NMR spectra of 100 mM of H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·26H<sub>2</sub>O prepared by method A (in D<sub>2</sub>O, 25 °C).

## 2. Results and discussion

Table 1 shows the carboxylation of benzene (**1a**) to benzoic acid (**2a**) with CO and O<sub>2</sub> catalyzed by Pd(OAc)<sub>2</sub> and H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·*n*H<sub>2</sub>O (HPMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·*n*H<sub>2</sub>O) prepared by various methods.

**1a** (2 mmol) was allowed to react under a mixed gas of CO (0.5 atm) and O<sub>2</sub> (0.5 atm) in the presence of catalytic amounts of Pd(OAc)<sub>2</sub> (0.1 mmol) and H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·*n*H<sub>2</sub>O (0.04 mmol) in acetic acid (5 mL) at 90 °C for 15 h. It was found that the carboxylation of **1a** is considerably affected by the preparation method of HPMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·*n*H<sub>2</sub>O. Fig. 1 shows the <sup>31</sup>P-NMR spectrum of H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·26H<sub>2</sub>O (**A**) prepared from H<sub>3</sub>PO<sub>4</sub>, MoO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub> by the Grate method [10].

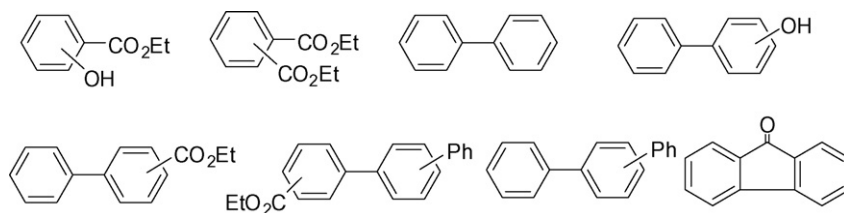
This shows a mixture of several molybdovanadophosphates with varying content of molybdenum and vanadium. It is well known that five geometrical isomers are present in the

H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·26H<sub>2</sub>O (**A**) and are difficult to separate from each other [10b,11]. The assignment of the <sup>31</sup>P-NMR spectrum was made by comparing the peaks with those of literature data [10b,12].

The reaction of **1a** with Pd(OAc)<sub>2</sub> combined with the catalyst **A** followed by esterification with ethanol afforded **2a** as an ethyl ester in 26% yield and a complex mixture of dimeric and polymeric products at 50% conversion of **1a** (entry 1). After esterification of these products with ethanol, their structures were identified by GC and GC–MS spectra (Scheme 1). Total yields of these products were estimated at 5% and most of the residue was found to be polymeric products.

When the reaction was prolonged to 60 h, the yield of **2a** increased to 42% yield at 90% conversion of **1a** (entry 2). It is interesting to note that the same reaction carried out by using H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·15H<sub>2</sub>O (**B**) prepared from Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>MoO<sub>4</sub>, and NaVO<sub>3</sub> by the Hallada method [13] gave phenol (**3a**) (2.9%) rather than **2a** (0.6%) as a major product, although the <sup>31</sup>P-NMR spectrum of **B** was almost the same as that of **A** (entry 3). In order to examine the effect of the crystal water in **B** on the carboxylation, we prepared H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>·22H<sub>2</sub>O (**C**) by the Hallada method and examined the carboxylation by the use of the catalyst **C**. However, **C** gave a result similar to **B** (entry 4). This indicates that the reaction is not affected by the crystal water.

We next tried to purify the catalyst **B** by recrystallization in order to know the effect of the preparation method on the catalytic performance. The catalyst **B** (2.5 g) was dissolved in water (ca. 15 mL) at 40 °C and then the solution was allowed to stand



Scheme 1. Products (**4**) obtained by carboxylation of **1a** with CO and O<sub>2</sub>.

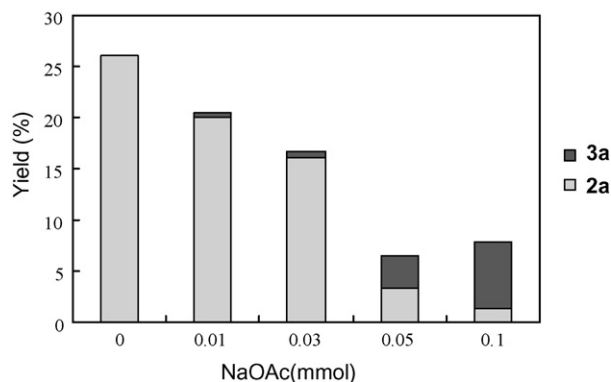


Fig. 2. Effect of AcONa on the reaction of **1a** by the catalyst **A** under the same conditions as entry 1 in Table 1.

at room temperature overnight to form  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 27\text{H}_2\text{O}$  (**D**) (1.7 g) as a light brown crystal. After removal of **D**, the filtrate was evaporated to dryness under reduced pressure to give a brown solid corresponding to  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 22\text{H}_2\text{O}$  (**E**). Thus, the reaction was examined by the use of the catalysts **D** and **E**. In contrast to entry 2 using the catalyst **B** where phenol **3a** was formed in preference to benzoic acid **2a**, the reaction by the purified catalyst **D** gave **2a** in 16% yield (entry 5), while the catalyst **E** recovered from the filtrate gave almost the same result as **B** did (entry 6). The fact that the carboxylation was rather improved by the use of the **D** obtained by recrystallization of **B** indicates that a certain impurity, which probably inhibits the carboxylation, is removed from the parent catalyst **B**. In fact, the reaction was inhibited by the catalyst **E** obtained from the filtrate containing the impurity. On the basis of these results, sodium ion seems to be a dominant candidate to inhibit the present carboxylation, since the  $\text{HPMo}_{10}\text{V}_2\cdot n\text{H}_2\text{O}$  prepared by the Hallada method is based on sodium salts of molybdenum and vanadium. In addition, by the catalyst **A** prepared by the Grate method from sodium-free materials,  $\text{H}_3\text{PO}_4$ ,  $\text{MoO}_3$ , and  $\text{V}_2\text{O}_5$ , promoted efficiently the carboxylation of **1a–2a** as shown in entry 1. These results suggest that the sodium ion appears to inhibit the carboxylation and to control the selectivity of **1a** to **2a** or **3a**.

In order to obtain further insight into the effect of the sodium ion on the present reaction, we conducted the reaction by adding AcONa to the catalyst **A** under the same conditions as entry 1 in Table 1 (Fig. 2).

It is interesting that the reaction caused by  $\text{Pd}(\text{OAc})_2$  combined with the catalyst **A** was found to be markedly influenced by adding AcONa, and the formation of phenol **3a** was increased with increase in the additive AcONa, in contrast to the decrease in the formation of benzoic acid **2a**. These results indicate that the sodium ion affects considerably the catalytic activity of the  $\text{Pd}(\text{OAc})_2/\text{HPMo}_{10}\text{V}_2$  catalytic system. In a previous paper, we reported that the direct hydroxylation of benzene **1a** to phenol **3a** by  $\text{H}_7\text{PMo}_8\text{V}_4\text{O}_{40}\cdot n\text{H}_2\text{O}$  is facilitated in the presence of a small amount of AcONa under similar reaction conditions [14]. Therefore, the formation of phenol **3a** by the present catalytic system may be due to the catalysis of the  $\text{HPMo}_{10}\text{V}_2\cdot n\text{H}_2\text{O}$  in the presence of AcONa. It is thought that the C–H bond activa-

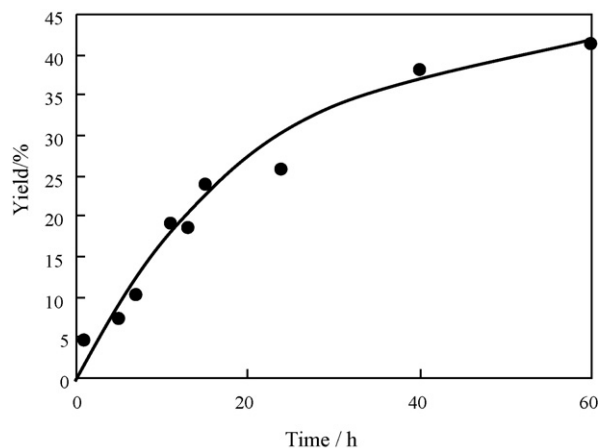


Fig. 3. Time-dependence curves for carboxylation of **1a** to **2a** by  $\text{Pd}(\text{OAc})_2/\text{HPMoV}$  under the same conditions as entry 1 in Table 1.

tion of benzene needed for the carboxylation by the Pd species becomes difficult to be induced by sodium ions.

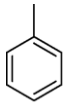
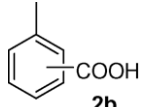
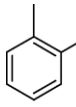
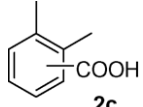
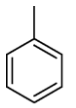
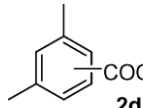
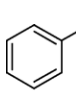
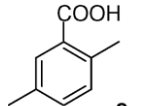
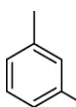
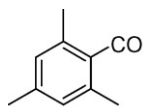
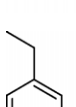
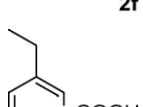
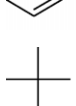
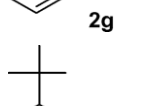
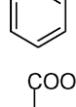
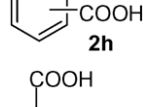
Fig. 3 shows the time-dependence curve of the carboxylation of **1a** to **2a** catalyzed by  $\text{Pd}(\text{OAc})_2$  and  $\text{HPMo}_{10}\text{V}_2\cdot 26\text{H}_2\text{O}$  (**A**) in acetic acid at  $90^\circ\text{C}$ .

From the time-dependence curve, it was found that the carboxylation proceeds relatively slowly and the selectivity of **1a–2a** was around 50% in the course of the reaction.

On the basis of these results, the carboxylation of alkylbenzenes **1** was carried out by using  $\text{Pd}(\text{OAc})_2$  and  $\text{HPMo}_{10}\text{V}_2\cdot 26\text{H}_2\text{O}$  (**A**) under various reaction conditions (Table 2).

Toluene (**1b**) was allowed to react under the same conditions as entry 1 in Table 1, forming the corresponding carboxylated products which consist of a regioisomeric mixture of *o*-**2b**, *m*-**2b**, and *p*-**2b** in a ratio of 17:32:52 in 41% yield (89% selectivity) at 48% conversion (entry 1). The selectivity in the carboxylation of **1b–2b** was higher than that of benzene **1a** to **2a**. This is believed to be due to the difficulty in forming dimeric products owing to its steric factor. To obtain the information of methyl substituents on the carboxylation, we conducted the reaction of *o*-, *m*-, and *p*-xylenes (**1c–e**) (entries 2–4). The reaction of **1c** gave 3,4-dimethylbenzoic acid (**2c<sub>3,4</sub>**) and 2,3-dimethylbenzoic acid (**2c<sub>2,3</sub>**) in a 90:10 ratio in 49% yield (89% selectivity). This shows that the geometry of the methyl group is a dominant factor to determine the regioselectivity of the carboxylation. The carboxylation of **1d** was found to be slightly difficult compared with that of **1c** to give a 62:38 mixture of 3,5- and 2,4-dimethylbenzoic acids (**2d<sub>3,5</sub>** and **2d<sub>2,4</sub>**) in 34% yield (87% selectivity) (entry 3). In contrast to the carboxylation of **1c** and **1d**, *p*-xylene (**1e**) afforded 2,5-dimethylbenzoic acid (**2e**) in a slightly lower selectivity (65%), probably because of the steric hindrance of the methyl substituent (entry 4). The carboxylation of 1,3,5-Trimethylbenzene (**1f**) was sluggish to form 2,4,6-trimethylbenzoic acid (**2f**) in low yield (14%) (entry 5). These results indicate that the geometry of methyl substituents on the benzene ring have a dominant factor to control both the reactivity and the selectivity of substrates in the present carboxylation. The carboxylation of ethylbenzene (**1g**) was similar

Table 2  
Carboxylation of alkylbenzenes with CO and O<sub>2</sub> by Pd(OAc)<sub>2</sub> combined with HPMo<sub>10</sub>V<sub>2</sub> (**A**) under various conditions<sup>a</sup>

Entry	Ar-H	AcOH (mL)	Temperature (°C)	Time (h)	Conversion (%)	Products yield (%) <sup>b</sup>
1	 <b>1b</b>	9	90	15	48	 <b>2b</b> 41 [89] <sup>c</sup> (17:32:51) <sup>d</sup>
2	 <b>1c</b>	9	90	15	55	 <b>2c</b> 49 [89] <sup>c</sup> (10:90) <sup>e</sup>
3	 <b>1d</b>	9	90	15	39	 <b>2d</b> 34 [87] <sup>c</sup> (0:62:38) <sup>f</sup>
4	 <b>1e</b>	9	90	15	40	 <b>2e</b> 26 [65] <sup>c</sup>
5	 <b>1f</b>	7	90	30	15	 <b>2f</b> 14 [93] <sup>c</sup>
6	 <b>1g</b>	7	90	15	42	 <b>2g</b> 35 [83] <sup>c</sup> (6:38:56) <sup>d</sup>
7	 <b>1h</b>	9	90	15	46	 <b>2h</b> 37 [83] <sup>c</sup> (0:46:54) <sup>d</sup>
8	 <b>1i</b>	1	110	15	68	 <b>2i</b> 46 [68] <sup>c</sup> (77:20:3) <sup>d</sup>

<sup>a</sup> **1** (2 mmol) was reacted under CO (0.5 atm) and O<sub>2</sub> (0.5 atm) by Pd(OAc)<sub>2</sub> (0.1 mmol) and HPMo<sub>10</sub>V<sub>2</sub> (0.04 mmol) in acetic acid (AcOH) at 90 °C for 15 h.

<sup>b</sup> GC yields.

<sup>c</sup> Selectivity (%) = yield of **2** (%) / conversion of **1** (%).

<sup>d</sup> Ratio of *ortho*:*meta*:*para* isomers.

<sup>e</sup> Ratio of 2,3- to 3,4-dimethylbenzoic acids.

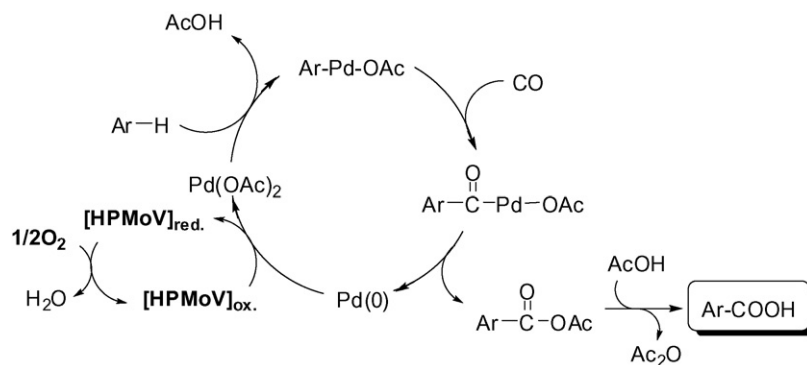
<sup>f</sup> Ratio of 2,6- to 3,5- to 2,4-dimethylbenzoic acids.

to that of toluene **1b** to lead to a 6:38:56 mixture of *o*-, *m*-, and *p*-ethylbenzoic acid (**2g**) in 35% yield (83% selectivity). In the carbonylation of *tert*-butylbenzene (**1h**), *m*- and *p*-*tert*-butylbenzoic acids (*m*-**2h** and *p*-**2h**) (46:54) were obtained in 37% yield (83% selectivity) as expected (entry 7). It is interesting to note that the regioselectivity in the carboxylation of benzoic acid (**1i**) was entirely different from that of alkylbenzenes to give phthalic acid (*o*-**2i**) in higher regioselectivity (entry 8). This indicates that the carboxyl group in **1i** triggers the present Pd-catalyzed carboxylation reaction. This effect based on the coordination of the substituent on the benzene ring is often observed in the Pd and Ru-catalyzed coupling reactions [15].

The present carboxylation of benzenes under CO and O<sub>2</sub> is considered to proceed through the following reaction path (Scheme 2).

The carboxylation is thought to proceed in a similar way to the carboxylation of anisole reported in our previous paper [8].

The reaction is initiated by the substitution of hydrogen on the benzene ring with Pd(OAc)<sub>2</sub> followed by the insertion of CO to form an aroylpalladium species. The subsequent reductive elimination of Pd(0) and aroyl acetate from the aroylpalladium species leads to benzoic acid. The Pd(0) is reoxidized by the action of [HPMo<sub>10</sub>V<sub>2</sub>]<sub>ox</sub>, and the reduced [HPMo<sub>10</sub>V<sub>2</sub>]<sub>red</sub> is reoxidized with O<sub>2</sub>.



Scheme 2. A plausible reaction path.

### 3. Experimental

#### 3.1. General

All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm  $\times$  25 m capillary column (BP-5).  $^1\text{H}$  and  $^{13}\text{C}$  NMR were measured at 270 and 67.5 MHz, respectively, in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  the internal standard.  $^{31}\text{P}$  NMR was measured at 109.25 MHz with 85%  $\text{H}_3\text{PO}_4$  in sealed capillary as the external standard. Heteropoly acids were prepared according to the method reported in literatures [10,11]. The crystal water content of the heteropoly acid was calculated according to DTA/TG.

#### 3.2. Preparation of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 26\text{H}_2\text{O}$ (A: by Grate method) [10]

To a suspension of  $\text{V}_2\text{O}_5$  (15 mmol, 2.73 g) and  $\text{MoO}_3$  (150 mmol, 2.16 g) in 50 mL of water, 85%  $\text{H}_3\text{PO}_4$  (15 mmol, 1.47 g) was added with stirring. The mixture was stirred at 130  $^\circ\text{C}$  for 2 h. After the reaction, the resulting red supernatant solution was decanted from gray solid. After evaporation of the solvent, the product was obtained by recrystallization from water.

#### 3.3. Preparation of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot n\text{H}_2\text{O}$ (B–E: by Hallada method) [11]

$\text{Na}_2\text{HPO}_4$  (5 mmol, 1.79 g) was dissolved in 10 mL of water and mixed with  $\text{NaVO}_3$  (20 mmol, 2.4 g) in 10 mL of water.  $\text{H}_2\text{SO}_4$  (0.5 mL) was added slowly to the reaction mixture. To this mixture was added  $\text{Na}_2\text{MoO}_4$  (55 mmol, 12.1 g) dissolved in 20 mL of water. Then,  $\text{H}_2\text{SO}_4$  (8.5 mL) was added slowly with vigorous stirring of the solution. After 10 min, the resulting red solution was extracted with 3  $\times$  20 mL of diethyl ether. The dark-red etherate layer was concentrated under reduced pressure to give the solid,  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 15\text{H}_2\text{O}$  (B). Addition of small amount of water (ca. 2 mL) to B (1.0 g) followed by evaporation under reduced pressure gave  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 22\text{H}_2\text{O}$  (C). The B (2.5 g) was dissolved in water (ca. 15 mL) at 40  $^\circ\text{C}$  and then the solution was allowed to stand at room temperature overnight to

form  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 27\text{H}_2\text{O}$  (D) (1.7 g) as a light brown crystal. After removal of the D, the filtrate was evaporated to dryness under reduced pressure to give a brown solid corresponding to  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 22\text{H}_2\text{O}$  (E).

#### 3.4. A typical procedure for the carboxylation of **1a**

To an AcOH solution (5 mL) of  $\text{Pd}(\text{OAc})_2$  (0.1 mmol) and  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot n\text{H}_2\text{O}$  ( $\text{HPMo}_{10}\text{V}_2$ ) (0.04 mmol) was added to **1a** (2 mmol). Then, the reaction mixture was stirred at 90  $^\circ\text{C}$  for 15 h under a 1:1 mixed gas (1 atm) of CO and  $\text{O}_2$ . After the reaction, the reaction mixture was subjected to GC measurement to estimate the conversion of **1a**. The reaction mixture was evaporated under reduced pressure to remove unreacted **1a** and acetic acid. The residue was extracted with 1 M NaOH (8 mL) and added isopropyl ether (5 mL). The water layer separated was acidified by aqueous  $\text{H}_2\text{SO}_4$  and then extracted with isopropyl ether. After evaporation of ether, the residue was subjected to esterification with ethanol (5 mL) acidified with  $\text{H}_2\text{SO}_4$  (0.1 g) under refluxing overnight. The evaporation of ethanol and then the distillation by Kugelrohr gave ethyl benzoate in 34% isolated yield. Products other than ethyl benzoate were determined by the GC and GC–MS analyses. The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC. The products were commercially available and the structures were confirmed by comparison of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

The compounds **2a** [16], **2b** [17], **2c–e** [18], **2f** [19], **2g–h** [16], **2i** [17], and **3a** [20] are known compounds and reported previously.

### Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformation of Carbon Resources” from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and “High-Tech Research Center” Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology, 2005–2009, and Daicel Chemical Industries Ltd.

## References

- [1] Y. Fujiwara, T. Kawauchi, H. Taniguchi, *J. Chem. Soc., Chem. Commun.* (1980) 220.
- [2] T. Jintoku, T. Taniguchi, Y. Fujiwara, *Chem. Lett.* (1987) 1159.
- [3] (a) T. Jintoku, Y. Fujiwara, I. Kawata, T. Kawauchi, T. Taniguchi, *J. Organomet. Chem.* 385 (1990) 297;  
(b) Y. Taniguchi, Y. Yamaoka, K. Nakata, K. Takaki, Y. Fujiwara, *Chem. Lett.* (1995) 345.
- [4] (a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* 34 (2001) 633;  
(b) Y. Fujiwara, K. Takaki, Y. Taniguchi, *Synlett.* (1996) 591.
- [5] K. Sakakibara, M. Yamashita, K. Nozaki, *Tetrahedron Lett.* 46 (2005) 959.
- [6] T. Yokota, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 67 (2002) 5005.
- [7] T. Yokota, M. Tani, S. Sakaguchi, Y. Ishii, *J. Am. Chem. Soc.* 125 (2003) 1476.
- [8] S. Ohashi, S. Sakaguchi, Y. Ishii, *Chem. Commun.* (2005) 486.
- [9] S. Yamada, S. Sakaguchi, Y. Ishii, *J. Mol. Catal. A: Chem.* 262 (2007) 48.
- [10] (a) J.H. Grate, D.R. Hamm, US Patent 5,792,721 (1998);  
(b) L. Pettersson, I. Andersson, J.H. Grate, A. Selling, *Inorg. Chem.* 33 (1994) 982.
- [11] (a) M.T. Pope, T.F. Scully, *Inorg. Chem.* 14 (1975) 953;  
(b) K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, *J. Mol. Catal. A: Chem.* 156 (2000) 143.
- [12] (a) M. Vennat, P. Herson, J.-M. Brégeault, G.B. Shul'pin, *Eur. J. Inorg. Chem.* (2003) 908;  
(b) A. Selling, I. Andersson, J.H. Grate, L. Pettersson, *Eur. J. Inorg. Chem.* (2000) 1509;  
(c) A.M. Khenkin, A. Rosenberger, R. Neumann, *J. Catal.* 182 (1999) 82;  
(d) I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171;  
(e) D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681;
- (f) A. Selling, I. Andersson, L. Pettersson, C.M. Schramm, S.L. Downey, J.H. Grate, *Inorg. Chem.* 33 (1994) 3141;
- (g) R. Neumann, M. Levin, *J. Am. Chem. Soc.* 114 (1992) 7278;
- (h) L.A. Combs-Walker, C.L. Hill, *Inorg. Chem.* 30 (1991) 4016;
- (i) K. Piepgrass, J.N. Barrows, M.T. Pope, *J. Chem. Soc., Chem. Commun.* (1989) 10;
- (j) M.A. Leparulo-Loftus, M.T. Pope, *Inorg. Chem.* 26 (1987) 2112;
- (k) A. Yagasaki, I. Andersson, L. Pettersson, *Inorg. Chem.* 26 (1987) 3926;
- (l) L. Pettersson, I. Andersson, L. Öhman, *Inorg. Chem.* 25 (1986) 4726;
- (m) J.A.R. Van Veen, O. Sudmeijer, C.A. Emeis, H. De Wit, *J. Chem. Soc., Dalton Trans.* (1986) 1825.
- [13] G.A. Tsigdinos, C.J. Hallada, *Inorg. Chem.* 7 (1968) 437.
- [14] M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi, Y. Ishii, *Angew. Chem. Int. Ed.* 44 (2005) 2586.
- [15] (a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kametani, M. Sonoda, N. Chatani, *N. Nat.* 366 (1993) 529;  
(b) F. Kakiuchi, Y. Yamamoto, N. Chatani, S. Murai, *Chem. Lett.* (1995) 681;  
(c) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* 35 (2002) 826;  
(d) M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Ohta, H. Takaya, R. Noyori, *J. Am. Chem. Soc.* 110 (1988) 629;  
(e) S. Bahmanyar, B.C. Borer, Y. Kim, D.M. Kurtz, S. Yu, *Org. Lett.* 7 (2005) 1011.
- [16] N. Hirai, N. Sawatari, N. Nakamura, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 68 (2003) 6587.
- [17] Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* 343 (2001) 393.
- [18] N. Hirai, Y. Tatsukawa, M. Kameda, S. Sakaguchi, Y. Ishii, *Tetrahedron* 62 (2006) 6695.
- [19] G.A. Olah, B. Török, J.P. Joschek, I. Bucsi, P.M. Esteves, G. Rasul, G.K.S. Prakash, *J. Am. Chem. Soc.* 124 (2002) 11379.
- [20] S. Mita, T. Sakamoto, S. Yamada, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* 46 (2005) 7729.