

# PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–heteropolyacids-catalyzed regioselective hydrocarboxylation of styrene

Bassam El Ali\*, Mohammed Fettouhi

*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

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## Abstract

The hydrocarboxylation of styrene has been carried out in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst and the heteropolyacids of general formula H<sub>3+n</sub>PMo<sub>12-n</sub>V<sub>n</sub>O<sub>40</sub> (HPA-*n*, *n* = 1–4) as co-catalyst in THF as solvent. The heteropolyacid H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> and HCl enhanced the catalytic reaction at 80 °C leading to excellent selectivity of branched aldehyde (>99%). The presence of HCl is essential for the achievement of the total conversion. No additional PPh<sub>3</sub> is needed with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrocarboxylation; Carbonylation; Palladium; Heteropolyacid; Styrene; Carboxylic acid

## 1. Introduction

The catalytic hydrocarboxylation of olefins, alkynes and other  $\pi$ -bonded compounds are reactions of important industrial potential [1–7]. Various transition-metal complexes such as palladium, rhodium, ruthenium or nickel complexes have been widely used in combination with phosphine and other types of ligands as catalysts in most carbonylation reactions [8–11]. The reactions of alkenes, alkynes and other related substrates with carbon monoxide in the presence of group VIII metals and a source of proton afford various carboxylic acids or carboxylic acid derivatives [1,3,5,6,8]. While many metals have been successfully employed as catalysts in these reactions, they often lead to mixtures of products under drastic experimental conditions [1,6,10,11].

The palladium-catalyzed hydrocarboxylation of alkenes has attracted considerable interest in recent

years. Aromatic carboxylic acids represent an important class of chemicals used mainly as anti-inflammatory agents. In general, the use of palladium systems in the presence of mono- or bidentate phosphine ligands and carbon monoxide in acidic medium led to the formation of a mixture of branched and linear acids [12].

The hydrocarboxylation of 4-methylstyrene has been studied using a homogeneous catalyst system of PdCl<sub>2</sub>–CuCl<sub>2</sub>–PPh<sub>3</sub> forming the branched carboxylic acid as a major product [13a]. Recently, interesting catalytic systems for the hydrocarboxylation of aryl alkenes including Pd/C or PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/*p*-TsOH/LiCl at 115 °C were described by Chaudhari and coworkers [13b,13c] claiming high yields and excellent selectivity (>99%). The need for alternative catalysts in the selective hydrocarboxylation of alkenes has led to the development of other palladium systems. For instance, we have previously described the hydrocarboxylation of alkenes using palladium(II) acetate/oxalic acid systems in the presence of a chelating phosphine ligand [14,15].

\* Corresponding author.

*E-mail address:* belali@kfupm.edu.sa (B. El Ali).

The hydrocarboxylation of alkenes is very sensitive to the reaction conditions. The systematic study and the modification of the reaction conditions represent crucial steps in the determination of the catalytic system. The stability of the active catalytic intermediate during the catalytic reaction is essential in minimizing the formation of metallic palladium. In this paper, we would like to describe the positive effect of the addition of the heteropolyacids as co-catalysts in the hydrocarboxylation of styrene catalyzed by  $\text{PdCl}_2(\text{PPh}_3)_2$  in the presence of HCl.

## 2. Experimental

### 2.1. Introduction

Styrene, solvents, phosphine ligands, and carboxylic and mineral acids are commercially available materials. The heteropolyacids  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  are also commercially available catalysts. The polyoxometallates  $\alpha_2\text{-K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Cu}^{2+}\cdot\text{OH}_2)\cdot 16\text{H}_2\text{O}$  and  $\alpha_2\text{-K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Ni}^{2+}\cdot\text{OH}_2)\cdot 16\text{H}_2\text{O}$  were synthesized following the method described in literature [17]. The other polyoxometallates  $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ ,  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ,  $\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$  and  $(\text{NH}_4)_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  were prepared according to the literature method [18]; however,  $\text{H}_7\text{PMo}_8\text{V}_4\text{O}_{40}$  was prepared according to the method described by Bregeault and coworkers [19]. The FT-IR spectra of the synthesized heteropolyacids did not show clear differences and the bands between 800 and  $1100\text{ cm}^{-1}$  confirmed the presence of the Keggin-type structure [20].

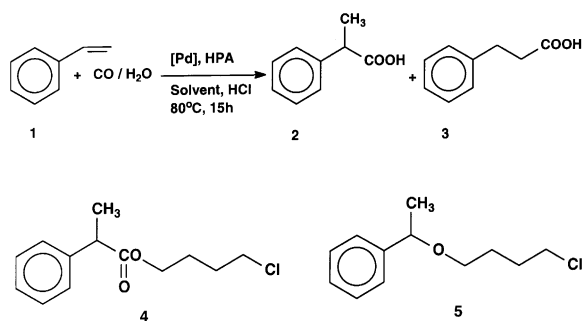
### 2.2. General procedure for the hydrocarboxylation of styrene

To a mixture of  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol) and HPA-2 (0.02 mmol) in THF (2.5 ml) was added styrene (2.0 mmol), water (10.0 mmol) and 35% HCl (0.10 ml). The mixture was placed in a glaze liner of a 45 ml autoclave. The autoclave was purged three times with 100 psi of carbon monoxide (CO) and then pressurized to 600 psi at room temperature. The system was heated ( $110^\circ\text{C}$ ) in an oil bath. After 15 h the reaction was cooled to room temperature, filtered

two times through celite and the mixture was then transferred to a 125 ml separatory funnel. A volume of 15 ml of ether and 15 ml of 3 M  $\text{NaHCO}_3$  were added to the mixture. The organic phase, separated from the aqueous phase, was dried over  $\text{Na}_2\text{SO}_4$  and analyzed by GC in the presence of 100  $\mu\text{l}$  of *p*-chloroanisole as internal standard to determine the conversion of styrene and the amount of byproducts. The aqueous phase was acidified by concentrated HCl and extracted with ether ( $3 \times 15\text{ ml}$ ). The ether was dried over  $\text{Na}_2\text{SO}_4$  and then evaporated to give the carboxylic acids **2** and **3** as pure products. The mixture was analyzed by  $^1\text{H NMR}$  to determine the ratio **2/3**. The products **2** and **3** gave excellent spectral data compared to authentic samples.

## 3. Results and discussion

The hydrocarboxylation of styrene was studied in the presence of  $\text{PdCl}_2(\text{PPh}_3)_2$  and heteropolyacids. The optimization of the reaction conditions was realized by studying the effects of the amount of HPA, the types of HPA, the amount and the type of acid, as well as other important factors that control the conversion and the selectivity of the reaction. The hydrocarboxylation of styrene **1** leads as expected to two major products **2** and **3** (Eq. (1)):



### 3.1. Effect of the amount of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot x\text{H}_2\text{O}$

We have started the study of the hydrocarboxylation of styrene with the effect of the amount of the co-catalyst under the optimized reaction conditions. Previously, a catalytic system including  $\text{PdCl}_2\text{-CuCl}_2\text{-PPh}_3\text{-HCl-H}_2\text{O}$  was described at

Table 1  
Effect of the amount of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 30\text{H}_2\text{O}$  (HPA-2)<sup>a</sup>

Run	HPA-2 (mmol)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	0	90	74	99.5/0.5	14	5
2	0.0030	100	80	99.4/0.6	4	7
3	0.0050	100	84	99.5/0.5	4	4
4	0.010	100	87	99.3/0.7	5	3
5	0.020	100	90	99.5/0.5	3	4
6	0.030	100	83	99.3/0.7	6	2
7	0.050	73	60	99.4/0.6	2	9

<sup>a</sup> Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml  $\approx$  1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

100 °C and 41 bar of CO in THF as solvent [2]. It was observed that the conversion and the selectivity were improved as the reaction temperature and pressure increased. Thus it appeared that the hydrocarboxylation of styrene with CO and water generally required severe reaction conditions. However, efficient hydrocarboxylation under mild conditions can be achieved in the presence of other co-catalysts such as heteropolyacids and also after tuning the reaction conditions.

The heteropolyacids of general formula  $\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}\cdot x\text{H}_2\text{O}$  (HPA-*n*) were used as co-catalysts of the reaction.  $\text{PdCl}_2(\text{PPh}_3)_2$  was adopted along with  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  (HPA-2) and 0.1 ml of HCl to start the optimization of the reaction conditions. The results given in Table 1 and Fig. 1 showed the positive effect of HPA-2 on the yield of the reaction. The carboxylic ester 4 and the ether 5 were identified as byproducts in THF as a solvent. The byproducts 4 and 5 were formed by the reaction of the carboxylic acid 2 and styrene with  $\text{Cl}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$ , respectively. This later was formed by the well-known reaction of THF with HCl.

The yield increased from 74 to 90% with the addition of 0.02 mmol of HPA-2 as co-catalyst (Table 1, entries 1–5). Further increase in the amount of HPA-2 to 0.030 and 0.05 mmol decreased the total yield of acids to 83 and 60%, respectively, by forming a significant amount of the byproducts 4 and 5 and other unidentified byproducts. Extremely high selectivity (>99%) toward branched carboxylic acid 2 was obtained in all cases.

### 3.2. Effect of the type of co-catalyst

Other co-catalysts such as the heteropolyacids  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  were used instead of HPA-2 (Table 2, entries 1–3) gave lower yields. However, the presence of vanadium in the structure of the heteropolyacid has improved significantly the yields of the carboxylic acids (Table 2, entries 4–7). Also the use of some polyoxoanions such as  $\alpha_2\text{-K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Cu}^{2+}\cdot\text{OH}_2)\cdot 16\text{H}_2\text{O}$  and  $\alpha_2\text{-K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Ni}^{2+}\cdot\text{OH}_2)\cdot 16\text{H}_2\text{O}$  as co-catalyst

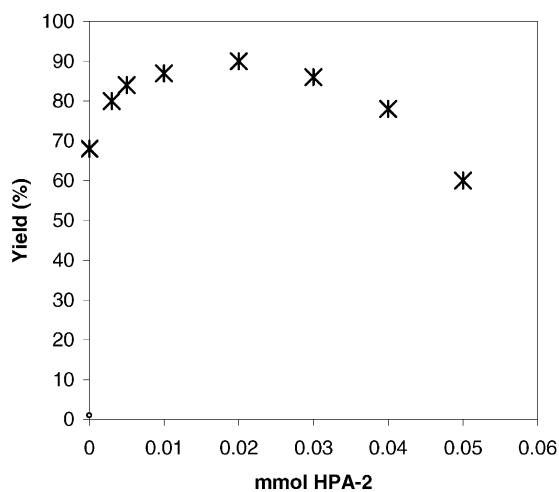


Fig. 1. Effect of the amount of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot 30\text{H}_2\text{O}$  (HPA-2) on the yield. Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml  $\approx$  1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

Table 2  
Effect of varying the type of co-catalyst<sup>a</sup>

Run	Co-catalyst	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> ( <b>2</b> + <b>3</b> ) (%)	Ratio <sup>d</sup> <b>2/3</b> (%)	Yield <sup>b</sup> <b>4</b> (%)	Yield <sup>b</sup> <b>5</b> (%)
1	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	97	79	99.5/0.5	8	6
2	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	98	75	99.4/0.6	13	7
3	H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	96	83	99.5/0.5	7	3
4	H <sub>4</sub> PMo <sub>11</sub> V <sub>1</sub> O <sub>40</sub>	96	85	99.3/0.7	5	4
5	H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	100	90	99.5/0.5	3	4
6	H <sub>5</sub> PMo <sub>9</sub> V <sub>3</sub> O <sub>40</sub>	100	88	99.3/0.7	5	3
7	H <sub>6</sub> PMo <sub>8</sub> V <sub>4</sub> O <sub>40</sub>	100	88	99.4/0.6	4	3
8 <sup>e</sup>	KPWCu	97	73	99.6/0.4	15	6
9 <sup>e</sup>	KPWNi	98	70	99.4/0.6	14	9
10 <sup>f</sup>	NH <sub>4</sub> VO <sub>3</sub>	100	77	99.6/0.4	11	12
11 <sup>g</sup>	NH <sub>4</sub> VO <sub>3</sub> /H <sub>3</sub> PO <sub>4</sub>	100	75	99.3/0.7	11	14
12 <sup>f</sup>	VO(AcAc) <sub>2</sub>	100	79	99.5/0.5	12	9

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), co-catalyst (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (**2** + **3**).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

<sup>e</sup> KPWCu: α<sub>2</sub>-K<sub>8</sub>P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>(Cu<sup>2+</sup>·OH<sub>2</sub>)·16H<sub>2</sub>O; KPWNi: α<sub>2</sub>-K<sub>8</sub>P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>(Ni<sup>2+</sup>·OH<sub>2</sub>)·16H<sub>2</sub>O.

<sup>f</sup> NH<sub>4</sub>VO<sub>3</sub> or VO(AcAc)<sub>2</sub> (0.04 mmol).

<sup>g</sup> NH<sub>4</sub>VO<sub>3</sub> (0.04 mmol)/H<sub>3</sub>PO<sub>4</sub> (0.02 mmol).

decreased the yields of the reaction (Table 2, entries 8 and 9). The use of vanadium(IV) complex VO(AcAc)<sub>2</sub> or vanadium(V) complex NH<sub>4</sub>VO<sub>3</sub> alone or with H<sub>3</sub>PO<sub>4</sub> gave lower yields of product compared to **HPA-2** (Table 2, entries 10–12). In general, the selectivity toward **2** was always maintained extremely high. The role of **HPA-2** in the reaction catalyzed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is probably to stabilize the palladium(II) intermediate and/or to reoxidize Pd(0) to active Pd(II) due to the presence of V(V).

### 3.3. Effect of the amount of the acid

HCl has also been reported as an absolutely necessary promoter in hydrocarboxylation [1,2], although, in hydrocarboxylation of alkenes, its addition resulted in the formation of undesired products. The effect of the amount of HCl is shown in Table 3 and Fig. 2. Very small amount of product was formed in the absence of HCl with or without addition of the heteropolyacid **HPA-2** (Table 2, entries 1 and 2). Significant

Table 3  
Effect of the amount of HCl<sup>a</sup>

Run	35% HCl ml (mmol)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> ( <b>2</b> + <b>3</b> ) (%)	Ratio <sup>d</sup> <b>2/3</b>	Yield <sup>b</sup> <b>4</b> (%)	Yield <sup>b</sup> <b>5</b> (%)
1 <sup>e</sup>	0	2	2	99.5/0.5	0	0
2	0	15	15	99.4/0.6	0	0
3	0.05 (0.40)	34	34	99.5/0.5	0	0
4	0.10 (1.1)	100	90	99.5/0.5	3	4
5	0.15 (1.65)	100	85	99.4/0.6	10	4
6	0.20 (2.20)	100	83	99.3/0.7	12	2
7	0.25 (2.75)	100	74	99.4/0.6	18	9
8	0.30 (3.30)	72	38	99.3/0.7	22	8

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (**2** + **3**).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

<sup>e</sup> No HPA-2 was added.

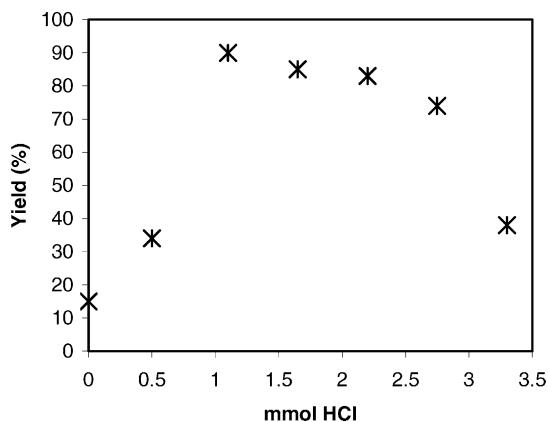


Fig. 2. Effect of the amount of HCl on the yield. Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

improvement in the yield of the reaction varied from 15 to 90% was achieved by adding HCl (Table 3, entries 3–5). The best results (100% conversion, 90% isolated yield) were obtained with 0.10 ml (1.1 mmol) of HCl (Table 3, entry 4, Fig. 2). The optimal molar ratio styrene/HCl/ $\text{PdCl}_2(\text{PPh}_3)_2$  equals to 400/220/1 was employed. The use of an excess of HCl versus styrene decreased the yield of the carboxylic acid as low as 38% (Table 3, entries 5–8).

The role of HCl in hydrocarboxylation was described as a source of the anionic ligand  $\text{Cl}^-$  [16], or as a reagent to form the chloro-compound,  $\text{Ph-CH}(\text{Cl})\text{CH}_3$ , as an intermediate in the process [13b,13c]. We have not identified any traces of the above-mentioned chloro-compound among the products or the byproducts of the reaction. Therefore, we believe that the main role of HCl is to provide  $\text{Cl}^-$  as an anionic ligand to the palladium complex.

### 3.4. Effect of the type of acid

The effect of the addition of other organic and mineral acids was tested in order to clarify the effect of HCl. Table 4 shows that only HCl has a promotional effect (entry 8). The conversion was significantly reduced by the addition of organic acids such as  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{SO}_3\text{H}$  or  $p\text{-TsOH}$  (Table 4, entries 1–4), as well as with mineral acids like  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  (Table 4, entries 5 and 6), and only traces of products were obtained with HI. Hence, the proton did not play a major role in the hydrocarboxylation. In addition, the reaction did not occur in the presence of 1.1 mmol of LiCl alone as additive (Table 4, entry 9). However, the use of  $\text{H}_2\text{SO}_4$  or a low concentration of HCl with LiCl (Table 4, entries 10 and 11) improved the conversion and the selectivity of the reaction and

Table 4  
Effect of the type of acid<sup>a</sup>

Run	Acid	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	$\text{HCOOH}$	5	5	99.5/0.5	0	0
2	$\text{CH}_3\text{COOH}$	9	9	99.5/0.5	0	0
3	$\text{CH}_3\text{SO}_3\text{H}$	7	7	99.5/0.5	0	0
4	$p\text{-TsOH}$	6	6	99.4/0.6	0	0
5	$\text{H}_2\text{SO}_4$	8	8	99.5/0.5	0	0
6	$\text{HNO}_3$	11	11	99.5/0.5	0	0
7	HI	Traces	Traces	–	0	0
8	HCl	100	90	99.5/0.5	3	4
9 <sup>e</sup>	LiCl	Traces	Traces	–	–	–
10 <sup>f</sup>	$\text{H}_2\text{SO}_4 + \text{LiCl}$	55	40	99.4/0.6	8	4
11 <sup>g</sup>	HCl + LiCl	85	76	99.5/0.5	6	4

<sup>a</sup> Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), HPA-2 (0.02 mmol), ligand (0.01 mmol), styrene (2.0 mmol), water (10.0 mmol), acid (1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using  $p$ -chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by  $^1\text{H}$  NMR.

<sup>e</sup> 1.10 mmol of LiCl.

<sup>f</sup> 1.10 mmol of  $\text{H}_2\text{SO}_4$  + 1.1 mmol of LiCl.

<sup>g</sup> 0.4 mmol of HCl + 1.1 mmol of LiCl.

Table 5

Effect of the amount of water<sup>a</sup>

Run	H <sub>2</sub> O (mmol)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>d</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	2.5	90	80	99.5/0.5	4	4
2	5.0	98	90	99.6/0.4	2	4
3	7.5	99	90	99.4/0.6	3	5
4	10.0	100	90	99.5/0.5	3	0
5	15.0	75	72	99.3/0.7	1	0
6	20.0	67	63	99.4/0.6	0	2

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

the yields of the products were increased to 40–85%. These results explained the essential role of HCl as a source of H<sup>+</sup> and Cl<sup>-</sup> to form the chloro-palladium hydride believed to be the key intermediate.

### 3.5. Effect of the amount of water

The amount of water in the reaction mixture had a crucial role on the conversion and the yield as shown in Table 5 and Fig. 3. When less than 5 mmol of water was used per 2 mmol of styrene, the conversion of styrene was high (90%), but the yield of carboxylic acid was 80% (Table 5, entry 1). As the amount of water increased, the isolated yield of acid showed a maximum at about 10 mmol and then the conversion

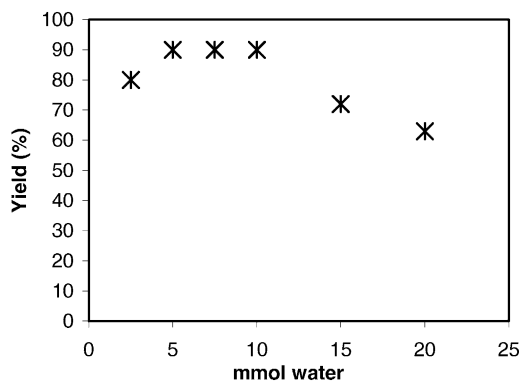


Fig. 3. Effect of the amount of water on the yield. Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

and the yield rapidly dropped. The high selectivity obtained for branched acid was independent to the amount of water.

### 3.6. Effect of temperature

Table 6 and Fig. 4 show the effect of the reaction temperature on the conversion and the selectivity of hydrocarboxylation under the optimized conditions (600 psi, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/HPA-2 = 1/4, H<sub>2</sub>O/styrene = 5) and with the addition of 0.1 ml HCl for 15 h. Thus, 100% conversion of styrene was obtained at temperature ≥ 80 °C (Table 6, entries 3–6). Both conversion and yield of the reaction were deteriorated

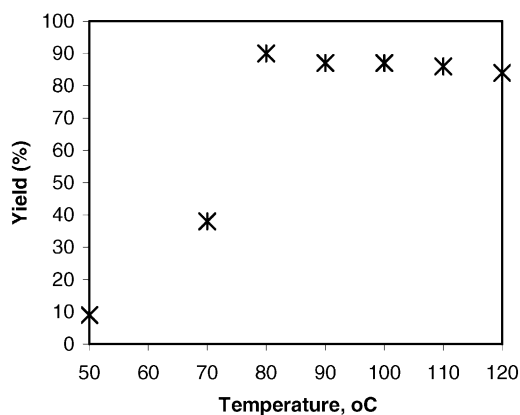


Fig. 4. Effect of the temperature on the yield. Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (0.10 ml), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 15 h.

Table 6  
Effect of temperature<sup>a</sup>

Run	T (°C)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	50	9	9	99.5/0.5	0	0
2	70	41	38	99.4/0.6	1	0
3	80	100	90	99.5/0.5	3	4
4	100	100	87	99.4/0.6	7	3
5	110	100	86	99.3/0.7	8	4
6	120	100	84	99.2/0.8	9	5

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (0.10 ml), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

Table 7  
Effect of reaction time<sup>a</sup>

Run	Time (h)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	3	13	13	99.6/0.4	0	0
2	6	70	64	99.5/0.5	4	2
3	9	88	82	99.4/0.6	3	3
4	12	100	88	99.5/0.5	5	4
5	15	100	90	99.5/0.5	3	4
6	18	100	89	99.3/0.7	3	5
7 <sup>e</sup>	3	100	82	99.5/0.5	7	8
8 <sup>e</sup>	6	100	80	99.4/0.6	9	7

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

<sup>e</sup> 100 °C.

when the temperature was further decreased (Table 6, entries 1 and 2). The highest yield (90%) of product was achieved at 80 °C (Table 6, entry 3 and Fig. 4). Again the selectivity to the branched acid was always maintained extremely high (≥99%).

### 3.7. Effect of the reaction time

The hydrocarboxylation of styrene at 80 °C is a relatively slow reaction. Table 7 and Fig. 5 showed the effect of the reaction time on the conversion of styrene and the yield of carboxylic acid. The best yield and conversion were achieved after 15–18 h of reaction (Table 7, entries 5 and 6; Fig. 5). Only 13% of product was formed after 3 h (Table 7, entry 1). The yield increased with the time of the reaction (Table 7, entries 2–6). The total conversion and the maximum of

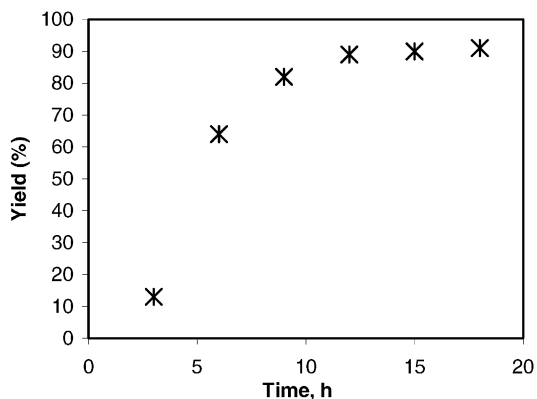


Fig. 5. Effect of reaction time on the yield. Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C.

Table 8  
Effect of the volume of THF<sup>a</sup>

Run	THF (ml)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	2.5	100	90	99.5/0.5	3	4
2	5.0	98	88	99.4/0.6	2	6
3	7.5	90	83	99.4/0.6	2	5
4	10	72	68	99.3/0.7	0	4
5	12.5	48	46	99.5/0.5	0	2
6	15	2	2	99.3/0.7	0	5

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

isolated yield (90%) were achieved after 15 h (Table 7, entry 5). It is worth noting that the total conversion of the styrene can be obtained at 100 °C after only 3–6 h of the reaction; however, the isolated yield of acid decreased to 80–82% due to the formation of byproducts (Table 7, entries 7 and 8).

### 3.8. Effect of the volume of solvent

The amount of solvent has a clear effect on the effectiveness of the catalytic system (Table 8 and Fig. 6). THF was among the preliminary tested solvent to give good results. At volumes of THF ranging between 2.5 and 7.5 ml, the total conversion of

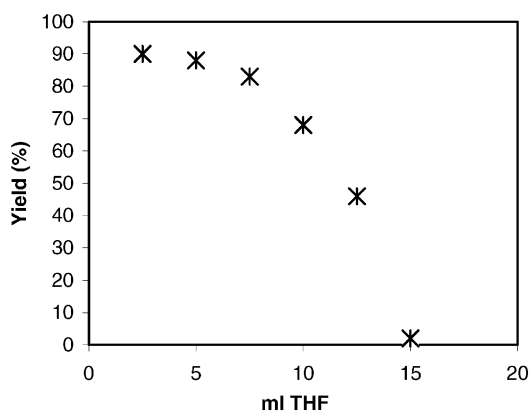


Fig. 6. Effect of the volume of THF on the yield. Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), 600 psi, 80 °C, 15 h.

styrene and the maximum yields of acid were obtained (Table 8, entries 1–3). The reaction became much slower at a volume of THF higher than 10 ml and the conversions in 10, 12.5 and 15 ml were 72, 48 and 2%, respectively (Table 8, entries 4–6). The results obtained are in contradiction with those observed with PdCl<sub>2</sub>/CuCl<sub>2</sub>/HCl/CO/H<sub>2</sub>O/THF at 100 °C, where the amount of the employed solvent did not make much difference on the conversion [2]. The highest conversion and yield of the reaction were achieved in 2.5 ml of THF.

### 3.9. Effect of the type of solvent

The effect of various solvents on the hydrocarboxylation of styrene in the presence of the catalytic system PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/HPA-2/H<sub>2</sub>O/HCl/CO is shown in Table 9. THF, 1,2-dimethoxyethane (1,2-DME), 1,4-dioxane and 2-butanone were among the tested solvents in this reaction and gave excellent results (Table 9, entries 1–4). However, the maximum isolated yield of carboxylic acid (90%) was obtained in THF as solvent. The non-polar solvents such as toluene and *n*-hexane, and chlorinated solvents such as CH<sub>2</sub>Cl<sub>2</sub> were ineffective where only traces of products were observed. We believe that the effectiveness of solvent is in deep correlation its miscibility with water and the solubility of the co-catalyst **HPA-2**.

### 3.10. Effect of CO initial pressure

The effect of the initial pressure of carbon monoxide on the hydrocarboxylation of styrene has been



Table 9  
Effect of type of solvent<sup>a</sup>

Run	Solvent	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	THF	100	90	99.5/0.5	3	4
2	DME	90	86	99.4/0.6	0	0
3	1,4-Dioxane	90	85	99.1/0.9	0	0
4	2-Butanone	92	89	98.5/1.5	0	0
5	CH <sub>3</sub> NO <sub>2</sub>	15	13	99.2/0.8	0	0
6	Toluene	Traces	Traces	–	0	0
7	CH <sub>2</sub> Cl <sub>2</sub>	Traces	Traces	–	0	0
8	Hexane	Traces	Traces	–	0	0

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), solvent (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

carefully studied (Table 10 and Fig. 7). The conversion and the yield improved significantly with the increase of CO pressure. Only 42–54% conversions of styrene have been obtained at 100–200 psi (Table 10, entries 1 and 2). The conversion increased to 66 and 85% at 300 and 400 psi, respectively (Table 10, entries 3 and 4). A total conversion was observed at a pressure equal or higher than 500 psi of CO and the maximum yield (90%) of acid was obtained at 600 psi. Further increase in CO initial pressure did not make much difference in the yield of acid (Fig. 7).

### 3.11. Effect of the type of phosphine ligand

The hydrocarboxylation of styrene was carried out in presence of various monodentate and bidentate

phosphine ligands in order to improve the selectivity of carboxylic acids and to minimize the formation of the byproducts. The results are summarized in Table 11. The use of the monodentate phosphine ligands such as PPh<sub>3</sub>, P(*o*-Ptol)<sub>3</sub>, PCy<sub>3</sub> and P(OPh)<sub>3</sub> did not improve or decrease the outcome of the reaction (Table 11, entries 1–4). However, the presence of bidentate phosphine ligands such as 1,2-bis(diphenylphosphino)ethane (1,2-DPPE), 1,3-bis(diphenylphosphino)propane (1,3-DPPP), 1,4-bis(diphenylphosphino)butane (1,4-DPPB) or (*S,S*)-2,4-bis(diphenylphosphino)pentane [(*S,S*)-2,4-BDPP] inhibited totally the carbonylation reaction. Only traces of carboxylic acid were formed and the unreacted styrene was recovered. It seems that a palladium complex intermediate [(P–P)–PdCl<sub>2</sub>] with the bidentate

Table 10  
Effect of CO initial pressure<sup>a</sup>

Run	Pressure (psi)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	100	42	40	99.5/0.5	0	2
2	200	54	51	99.4/0.6	2	2
3	300	66	62	99.5/0.5	3	1
4	400	85	79	99.4/0.6	3	2
5	500	100	88	99.5/0.5	4	5
6	600	100	90	99.5/0.5	3	4

<sup>a</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

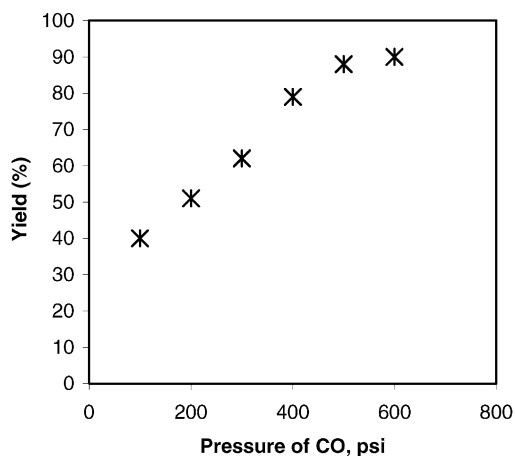


Fig. 7. Effect of CO initial pressure on the yield. Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml  $\approx$  1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

phosphine ligand is responsible for the inhibition of catalytic activity of palladium.

### 3.12. Effect of the type of palladium catalyst

The effect of the type of palladium catalysts has been carefully studied by using various palladium(II) and palladium(0) complexes in the presence and in the absence of  $\text{PPh}_3$  (Table 12). All palladium com-

plexes showed no catalytic activity in the absence of  $\text{PPh}_3$  (except  $\text{PdCl}_2(\text{PPh}_3)_2$ ). The ratio of Pd/ $\text{PPh}_3$  was maintained at 8. Total conversion of styrene was observed with all palladium complexes except with  $\text{Pd}(\text{CN})_2$  where the conversion was very low (20%) (Table 12, entry 9). The strong coordination ability of the cyanide ligand to the palladium inhibits the formation of the chlorophosphino palladium(II) complex as intermediate. All other palladium(II) complexes (Table 12, entries 2–5, 7 and 8) and Pd/C (Table 12, entry 10) gave excellent results.  $\text{Na}_2\text{PdCl}_4$  and the palladium(0) complexes such as  $\text{Pd}(\text{dba})_2$  showed also high catalytic activity (Table 12, entries 11 and 12).

### 3.13. Proposed mechanism

The mechanism of the hydrocarboxylation of styrene catalyzed by palladium(II) in the presence of HCl has not yet been totally clarified. Chaudhari and coworkers [13b,13c] described the role of HCl (formed in situ by the reaction of LiCl and *p*-TsOH) as the formation of  $\text{Ph}-\text{CH}(\text{Cl})\text{CH}_3$  as intermediate followed by the carbonylation in the presence of Pd(II). Our results, obtained with the catalytic system  $\text{PdCl}_2(\text{PPh}_3)_2/\text{HPA-2}/\text{CO}/\text{HCl}/\text{H}_2\text{O}$  at 80 °C, showed clearly the absolute need for both Cl and  $\text{PPh}_3$  on the palladium center. The following experiments (Eqs. (2)–(4)) involving  $\text{D}_2\text{O}$  and/or DCl have been

Table 11  
Effect of the type of phosphine ligand<sup>a</sup>

Run	Ligand	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	$\text{PPh}_3$	98	89	99.5/0.5	4	3
2	$\text{P}(o\text{-Tol})_3$	100	86	99.4/0.6	6	4
3	$\text{PCy}_3$	100	82	99.5/0.5	6	8
4	$\text{P}(\text{OPh})_3$	82	75	99.4/0.6	3	4
5 <sup>e</sup>	1,2-DPPE	Traces	Traces	–	–	–
6 <sup>e</sup>	1,3-DPPP	Traces	Traces	–	–	–
7 <sup>e</sup>	1,4-DPPB	Traces	Traces	–	–	–
8 <sup>e</sup>	( <i>S,S</i> )-2,4-BDPP	Traces	Traces	–	–	–

<sup>a</sup> Reaction conditions:  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.005 mmol), HPA-2 (0.02 mmol), ligand (0.04 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml  $\approx$  1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

<sup>e</sup> 1,2-DPPE: 1,2-bis(diphenylphosphino)ethane; 1,3-DPPP: 1,3-bis(diphenylphosphino)propane; 1,4-DPPB: 1,4-bis(diphenylphosphino)butane; (*S,S*)-2,4-BDPP: (*S,S*)-2,4-bis(diphenylphosphino)pentane.

Table 12  
Effect of the type of palladium catalyst<sup>a</sup>

Run	Catalyst	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (2 + 3) (%)	Ratio <sup>d</sup> 2/3	Yield <sup>b</sup> 4 (%)	Yield <sup>b</sup> 5 (%)
1	PdCl <sub>2</sub>	0	–	–	–	–
2	PdCl <sub>2</sub> /PPh <sub>3</sub>	99	85	99.5/0.5	6	4
3	PdBr <sub>2</sub> /PPh <sub>3</sub>	95	76	99.4/0.6	8	7
4	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	100	90	99.5/0.5	3	4
5	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> /PPh <sub>3</sub>	100	88	99.4/0.6	4	5
6	Pd(OAc) <sub>2</sub>	Traces	Traces	–	–	–
7	Pd(OAc) <sub>2</sub> /PPh <sub>3</sub>	100	79	99.1/0.9	6	8
8	Pd(NO <sub>3</sub> ) <sub>2</sub> /PPh <sub>3</sub>	100	80	99.2/0.8	7	9
9	Pd(CN) <sub>2</sub> /PPh <sub>3</sub>	20	15	99.2/0.8	1	3
10	Pd/C/PPh <sub>3</sub>	98	78	99.3/0.7	5	7
11 <sup>e</sup>	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	100	82	99.4/0.6	6	7
12	Na <sub>2</sub> PdCl <sub>4</sub> /PPh <sub>3</sub>	100	79	99.5/0.5	7	8

<sup>a</sup> Reaction conditions: Pd (0.005 mmol), PPh<sub>3</sub> (0.04 mmol), HPA-2 (0.02 mmol), styrene (2.0 mmol), water (10.0 mmol), 35% HCl (0.10 ml ≈ 1.10 mmol), THF (2.5 ml), 600 psi, 80 °C, 15 h.

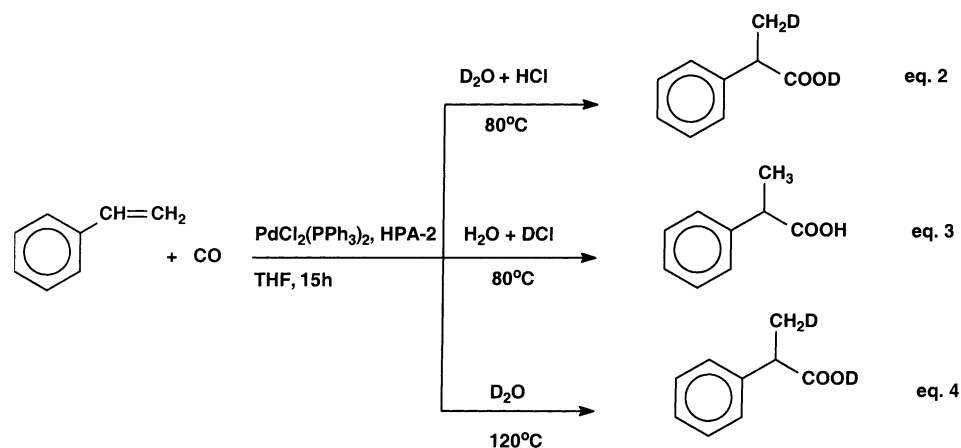
<sup>b</sup> Determined by GC using *p*-chloroanisole as internal standard.

<sup>c</sup> Isolated total yield (2 + 3).

<sup>d</sup> Determined by <sup>1</sup>H NMR.

<sup>e</sup> dba: Ph–CH=CHCOCH=CH–Ph.

carried out in order to clarify the mechanism of the reaction:



The major product (yield > 90%) of the reaction of carbonylation of styrene with D<sub>2</sub>O + HCl (80 °C) (Eq. (2)) or with D<sub>2</sub>O alone (120 °C) (Eq. (4)) indicated clearly that the deuterium D introduced on the terminal carbon of the double bond was most probably originated from D<sub>2</sub>O. In addition, the reaction with DCl + H<sub>2</sub>O gave only a deuterated minor product (yield < 10%) (Eq. (3)).

The structure of the final products including the H–H coupling and the integration of protons was carefully studied by <sup>1</sup>H NMR. A clear triplet (in place of

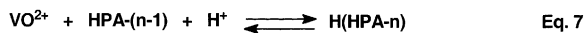
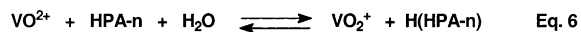
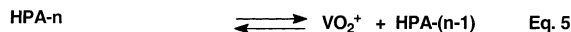
quartet) was obtained for ‘H’ of Ph–CH–CH<sub>2</sub>D in the product and the ratio of the integration of H (CH) and H (CH<sub>2</sub>D) was 1/2.

It was interesting to observe that the ‘H’ of HCl was not probably directly involved in the final product, which indicates that the role of the HCl is a source of Cl<sup>–</sup> ion. The anion Cl<sup>–</sup> is the ligand needed to stabilize a key chlorinated palladium intermediate in the hydrocarboxylation of styrene. It also seems that

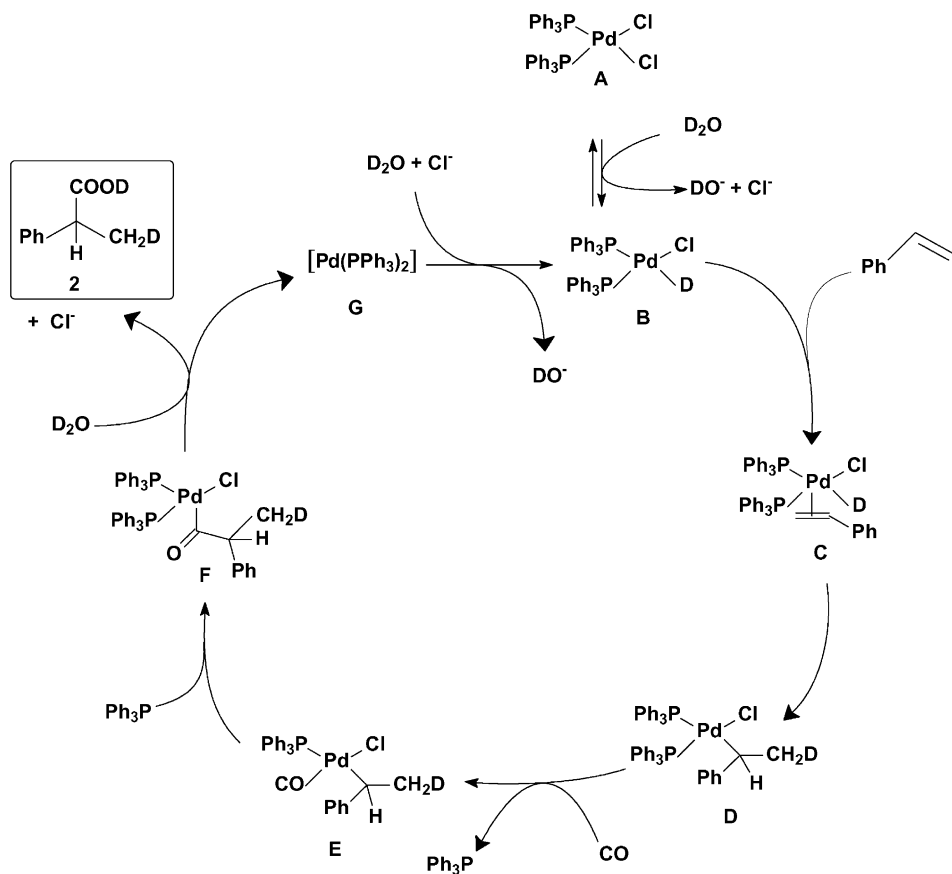
at least one  $\text{Cl}^-$  and one  $\text{PPh}_3$  are always present on the palladium center.

The role of the heteropolyacid in the hydrocarboxylation of styrene is secondary and its mechanism is not yet very clear. The attempts to isolate some intermediates or to analyze the solid at the end of the reaction have failed in providing clear information about a possible complexation between palladium and HPA-2. The IR spectra of the solid obtained from the reaction mixture exhibited the following skeletal vibrations: 1064, 960, 860 and 760 that are typical for the Keggin oxoanion structure. These major peaks were attributed to  $\nu(\text{P}-\text{O}_i-\text{Mo})$ ,  $\nu(\text{Mo}-\text{O}_t)$  and  $\nu(\text{Mo}-\text{O}_b-\text{Mo})$ , respectively [20]. These IR spectra indicated that the integrity of Keggin structure of the heteropolyacid was well conserved. We believe that  $\text{VO}_2^+$  present within the heteropolyacid structure is

the species responsible for the stabilization of the active palladium intermediate or in the reoxidation of some reduced palladium species.  $\text{VO}_2^+$ , the reduced form of  $\text{VO}_2^{2+}$ , is probably reoxidized in the presence of acid and  $\text{H}_2\text{O}$  (Eqs. (5)–(7)):



The results obtained with V(IV) (Table 2, entry 12) suggests that  $\text{VO}_2^+$  may also participate in the stabilization of the palladium active species. However, the mechanisms of the interaction between the heteropolyacid and palladium(II) are still not very



Scheme 1.

clear. More study is needed to clarify this important point.

A possible mechanism for this reaction is outlined in Scheme 1.  $D_2O$  reacts with palladium complex  $PdCl_2(PPh_3)_2$  (**A**) to form the active hydridopalladium complex (II) (**B**) followed by the coordination of styrene through **C** to give **D**. The deuterium is introduced into the terminal carbon of the double bond. The effect of coordination of styrene to palladium center via the internal carbon of the double bond is well known to be more electronic and less steric. The insertion of CO in place of  $PPh_3$  gives the chlorocarbonyl palladium complex **E**. The migratory insertion of CO into palladium–carbon bond in the presence of  $PPh_3$  gave the palladium(II) intermediate **F**. The last step of the mechanism involves a reductive elimination forming the carboxylic acid **2** and the palladium(0) intermediate **G**. The later undergoes the reaction with  $D_2O$  and  $Cl^-$  to regenerate the active intermediate species **B**.

#### 4. Conclusion

The results of our study clearly showed that the homogeneous catalytic system  $PdCl_2(PPh_3)_2/HPA-2/HCl/CO/H_2O$  in THF is an efficient system for the regioselective hydrocarboxylation of styrene leading to the branched carboxylic acid. We have shown in this study that the reaction is sensitive to the choice of the solvent, the amount of acid, the molar ratio of  $H_2O$ /styrene, CO pressure and the temperature of the reaction. The effect of HCl addition was essential in order to provide  $Cl^-$  and  $H^+$ . The mechanisms of the reaction involving the heteropolyacid are not yet clear. However, we believe that the role of the heteropolyacid HPA-2, due to the presence of V(V), is probably to stabilize the palladium(II) complex intermediate and/or to reoxidize palladium(0) formed during the reaction.

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