

# Biphasic carbonylation of vinyl aromatic compounds using novel water-soluble Pd catalyst: activity, selectivity and mechanistic studies

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## Abstract

The biphasic carbonylation of vinyl aromatic compounds to the isomeric arylpropanoic acids has been studied in detail using a novel water-soluble palladium complex,  $[\text{Pd}(\text{Pyca})(\text{TPPTS})]^+\text{TsO}^-$ . The effect of various reaction and catalyst parameters such as promoters, solvents, P/Pd ratio, CO partial pressure, temperature and concentration of substrate on the catalytic activity and selectivity has been investigated using styrene as the model substrate. High catalytic activity ( $\text{TOF} = 282 \text{ h}^{-1}$ ) and selectivity to the branched product ( $\sim 91\%$ ) was observed with  $[\text{Pd}(\text{Pyca})(\text{TPPTS})]^+\text{TsO}^-$  catalyst.  $^{31}\text{P}$  NMR experiments were carried out to study the mechanistic details and to understand the nature of catalytic species formed under the reaction conditions, based on which a plausible catalytic cycle has been proposed. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Biphasic; Hydrocarboxylation; Palladium; Vinyl aromatic compounds; Water-soluble complex; Catalysis

## 1. Introduction

The widespread application of homogeneous catalysis in C–C bond formation reactions [1,14] including carbonylation [2,15,16] is attributed to their high catalytic activity as well as high selectivity which are, in many cases, difficult to achieve by heterogeneous catalysis. Despite these advantages, the industrial applications of many of these processes were not realized due to the tedious separation processes and recycle of the precious catalysts. Hence, it has been a target of research during the last decade to heterogenize the homogeneous catalysts to incorporate the advan-

tages of homogeneous catalysis as well as the efficient catalyst–product separation. One of the many ways to achieve this goal is the use of biphasic catalyst systems in which the water-soluble catalyst can be easily separated from the organic-soluble products [3,17]. Higher catalytic activities were achieved in the case of water miscible organic substrates, whereas very low catalytic activities were obtained in the case of sparingly water-soluble or water-immiscible organic reactants due to transport limitation. Co-solvents [4] as well as catalyst binding ligands [5] were used to improve the catalytic activity in such cases. Both the approaches have their own limitations such as side reactions and recovery of the foreign substance from the product or catalyst phase, catalyst leaching, etc. Hence the focus was mainly to develop highly active and selective catalysts with modified ligands. Sulphonated

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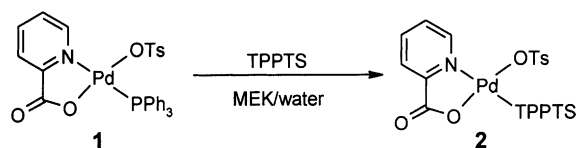
phosphines such as triphenylphosphine monosulphonate (TPPMS), triphenylphosphine trisulphonate (TPPTS) and bis[disulphonatophenylphosphinomethyltetrasulphonatobinaphthene] (BINAS) were the commonly used ligands to make the water-soluble palladium complexes for the carbonylation of organic halides, alcohols and olefins [6,18].

Carbonylation of vinyl aromatic compounds (Scheme 2) is an elegant and environmentally benign process for the synthesis of 2-arylpropionic acids, a class of non-steroidal anti-inflammatory agents. In general, homogeneous palladium complexes have been used for this conversion and their water-soluble analogues have been recently reported to facilitate efficient separation of the catalyst. Thus, biphasic carbonylation of styrene using in situ prepared Pd(TPPTS)<sub>3</sub> [8], as well as cationic water soluble Pd complexes containing bidentate xantphos ligands has been recently demonstrated [11]. However, in these cases, the catalytic activity (TOF = 1.5–50 h<sup>-1</sup>) as well as 2-arylpropanoic acid selectivity (35–70%) was found to be very low under relatively mild reaction conditions (323–393 K, 4–6 MPa). Thus it has been a prime concern to develop a catalyst system having high activity and selectivity. In the present work, the catalytic performance of a new water-soluble catalyst [Pd(Pyca)(TPPTS)](TsO) [Pyca: pyridine-2-carboxylato] for the carbonylation of styrene has been studied with respect to various reaction and catalyst parameters as CO partial pressure, reaction temperature, substrate concentration, TPPTS/Pd ratio, promoters, solvents, etc. It is shown that with this catalyst, a significantly higher activity and selectivity for the desired 2-arylpropanoic acid can be obtained. <sup>31</sup>P NMR experiments were carried out to investigate the nature of various catalytic species formed in solution under the reaction conditions.

## 2. Experimental

### 2.1. General

Styrene, *p*-toluenesulphonic acid monohydrate (Aldrich, USA), LiCl (S.d. Fine-chem., India) and CO (Matheson, USA, 99.9% purity) were used as received. All the solvents were freshly distilled using known procedures and degassed by argon before use.



Scheme 1. Synthesis of novel water-soluble palladium complex 2.

### 2.2. Synthesis of the water-soluble Pd complex Pd(Pyca)(TPPTS)(TsO) [9]

Complex 1 [10] was dissolved in methyl ethyl ketone (MEK) (10 ml) and shaken vigorously with 2 or 3 equiv. of TPPTS in water (6 ml). The yellow colour of the MEK layer disappeared and the aqueous layer became yellow indicating the formation of complex 2 in water (Scheme 1).

For the carbonylation reaction, the aqueous layer was used after washing with pure MEK a few times (traces of MEK remains in the aqueous layer). The complex 2 can be isolated from water by precipitation using ethanol. The yellow suspension of 2 was filtered under argon, washed with ethanol followed by diethyl ether and dried under vacuum to yield a fine yellow powder of the complex 2. Anal. calcd. for C<sub>31</sub>H<sub>23</sub>N Na<sub>3</sub>O<sub>14</sub>PPdS<sub>4</sub>·6H<sub>2</sub>O: C, 34.598; H, 3.278; N, 1.301; S, 11.916; P, 2.878; found: C, 34.05; H, 3.28; N, 1.33; S, 12.32; P, 2.50.

### 2.3. Carbonylation procedure

The reactions were carried out in a 50 ml Parr Autoclave made of Hastelloy C-276 having facilities for gas inlet and outlet, rupture disc as a safety measure in case of excessive pressure build up, intermediate sampling, temperature-controlled heating and variable agitation speed. For a typical biphasic carbonylation reaction, the autoclave was charged with the catalyst (prepared as per the above procedure) in 6 ml of water after making the total volume 25 ml with substrate dissolved in toluene, along with the promoters. The contents were flushed few times with nitrogen followed by carbon monoxide and heated to the desired temperature (under low stirring, 10–20 rpm). After attaining the temperature, the autoclave was pressurized with CO to the desired level, and the reaction started by starting agitation (1100 rpm). To maintain a constant pressure in the reactor, CO was fed

through a constant-pressure regulator from a reservoir vessel (100 ml). Pressure drop in the reservoir vessel was recorded by means of a pressure transducer as a function of time. Intermediate organic phase samples were also taken at regular intervals of time and were subjected to analysis to determine the conversion and selectivity at the given time, from which turnover frequency (TOF) and selectivity were calculated for that particular reaction time. After the reaction, the organic and aqueous layers were separated using a separating funnel and the organic layer was analysed for substrate and products using a gas chromatograph (HP 5890) having a HP-FFAP capillary column (length = 30 m). The carbonylation products were isolated by evaporation of the solvent and purified further by acid–base extraction. The products were further confirmed by NMR and IR analysis. However, the final conversion, selectivity, and TOF were calculated at the end of the reaction also. The conversion, TOF (averaged over the given reaction time) and selectivity were calculated as follows:

Net conversion = Initial concentration of styrene

– final concentration of (styrene + phenylethylchloride + phenylethanol)

$$\% \text{ Conversion} = \frac{\text{Net conversion}}{\text{Initial concentration of styrene}} \times 100$$

$$\% \text{ Selectivity of the product} = \frac{\text{Concentration of the product formed}}{\text{Net conversion}} \times 100$$

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{No. of moles of carbonylation products formed}}{\text{No. of moles of catalyst} \times \text{time in hours}}$$

#### 2.4. $^{31}\text{P}$ NMR experiments

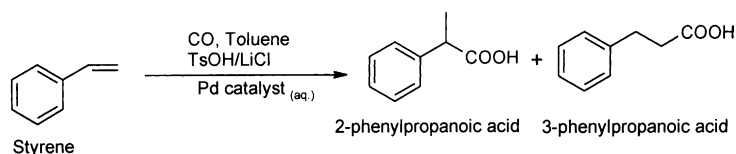
The  $^{31}\text{P}$  NMR spectra were recorded at 202.456 MHz by using 85%  $\text{H}_3\text{PO}_4$  as an external standard and  $\text{D}_2\text{O}$  (added in a capillary tube) as the deuterium source in a Bruker DRX-500 NMR Spectrometer.

### 3. Results and discussion

Hydrocarboxylation of vinyl aromatic compounds produces two isomeric arylpropanoic acids, namely 2- and 3-arylpropanoic acids, the selectivity of which depends on the catalyst system and reaction conditions employed. For convenience, styrene was used as a model substrate in the experiments, which leads to both 2- and 3-phenylpropanoic acids (Scheme 2). In this paper, experimental results on the biphasic carbonylation of styrene, using the aqueous catalyst  $[\text{Pd}(\text{Pyca})(\text{TPPTS})]^+(\text{TsO})^-$  together with free TPPTS in the presence of *p*-toluenesulphonic acid (*p*-TsOH) and lithium chloride (LiCl) promoters have been presented. The organic phase consists of styrene and the products using toluene as a solvent, while the catalyst and the promoters are present in the aqueous phase. The role of the solvents, promoters, CO pressure, P/Pd ratio, catalyst recycle, etc., in the biphasic carbonylation were investigated and the results are discussed as follows.

#### 3.1. Effect of solvents

In most liquid phase catalytic reactions, solvents can influence the rate of the reaction or selectivity due to solubility variations and in some cases by interaction



Scheme 2. Carbonylation of styrene.

Table 1  
Biphasic hydrocarboxylation of styrene<sup>a</sup>

Run	H <sup>+</sup> :Cl <sup>-</sup>	Solvent	Time (h)	Conversion (%)	TOF (h <sup>-1</sup> )	Selectivity <sup>b</sup> (%)	
						<i>iso</i> -Acid	<i>n</i> -Acid
1	11.2:11.2	Toluene	1.5	93	282	90.7	8.7
2	5.6:5.6	Toluene	3	65	99	90.3	9
3	2.3:2.3	Toluene	6	50	38	91	8.2
4 <sup>c,d</sup>	11.2:11.2	Toluene	4	30	34	41.2	58
5 <sup>e</sup>	11.2:11.2	Toluene	2.5	76.5	139	76.5	23
6 <sup>f</sup>	11.2:0	Toluene	3.5	78	102	41	59
7	11.2:11.2	MEK	1.5	80	244	78	22
8	11.2:11.2	Cyclohexane	3	70	106	92	8

<sup>a</sup> Reaction conditions: Pd, 0.0629 mmol; TPPTS/Pd: 3; substrate, 28.8 mmol; *p*-TsOH, 11.2 mmol; LiCl, 11.2 mmol; H<sub>2</sub>O, 6 ml; toluene, 15.5 ml; *P*<sub>CO</sub>, 54 bar; *T*, 388 K.

<sup>b</sup> Traces of bis( $\alpha$ -methylbenzyl)ether was also detected.

<sup>c</sup> Substrate: 57.7 mmol.

<sup>d</sup> Catalyst: PdCl<sub>2</sub>/4 equiv. of TPPTS.

<sup>e</sup> HCl instead of *p*-TsOH/LiCl.

<sup>f</sup> In the absence of LiCl.

with catalytic species. The effect of solvents on carbonylation of styrene was investigated in which organic solvents such as cyclohexane, MEK, and toluene were used. It was observed that toluene was the best with respect to catalytic activity (TOF = 282 h<sup>-1</sup>) and selectivity to 2-arylpropanoic acid (91%). The catalytic system was also stable under the reaction conditions as it showed only negligible Pd leaching (<0.05 ppm) in the toluene phase. In MEK as the solvent, though the reaction rates (Run 7, Table 1) were comparable with that in toluene, the selectivity to 2-arylpropanoic acid observed was lower. Also, leaching of palladium to the organic phase was observed in MEK as the solvent (~10 ppm). The reasons behind such variation may be due to the stability of the active intermediate species in the particular solvent system.

### 3.2. Role of promoters

The carbonylation of olefins using Pd complex catalysts is known to be facilitated in the presence of a Brønsted acid and halide promoters [12]. The acidic and halide promoters have a significant role on the biphasic carbonylation of styrene also. *p*-TsOH and LiCl are reported to give a stable catalyst system at a 1:1 ratio of *p*-TsOH to LiCl [13]. Experiments on carbonylation of styrene were carried out using different amount of the promoters (*p*-TsOH and LiCl)

keeping the ratio constant at 1:1, (Runs 1–3, Table 1) and it was observed that 11.2 mmol each of *p*-TsOH and LiCl gave the best activity (TOF = 282 h<sup>-1</sup>) and selectivity to 2-arylpropanoic acid (~91%) (Run 1, Table 1). The catalytic activity was found to increase with concentration of *p*-TsOH and LiCl (1:1) as shown in Fig. 1. In the absence of LiCl, the catalytic activity as well as the selectivity decreased considerably (Run 6, Table 1), suggesting a possible involvement of LiCl in the formation of phenyl ethyl chloride as the active substrate. The formation of phenyl ethyl chloride was also confirmed by the analysis of intermediate organic phase samples. In addition, a small amount of phenyl ethyl alcohol was also detected in the intermediate samples, which may have been formed by the acid catalysed reversible hydration of the olefin. However, in the final reaction mixture, only negligible amount of the alcohol was detected (Fig. 1).

In biphasic carbonylation reactions, the solubility of the organic substrate as well as the gaseous reactant (CO) in the aqueous catalytic phase is one of the most crucial factors, which affects the overall catalytic performance. Since, the chloro-intermediate is the active substrate in the present case, its formation also depends on the mutual solubility of the olefin and the promoters in aqueous and organic phases, respectively. *p*-TsOH, which also has good surfactant properties, may enhance miscibility of both the phases,

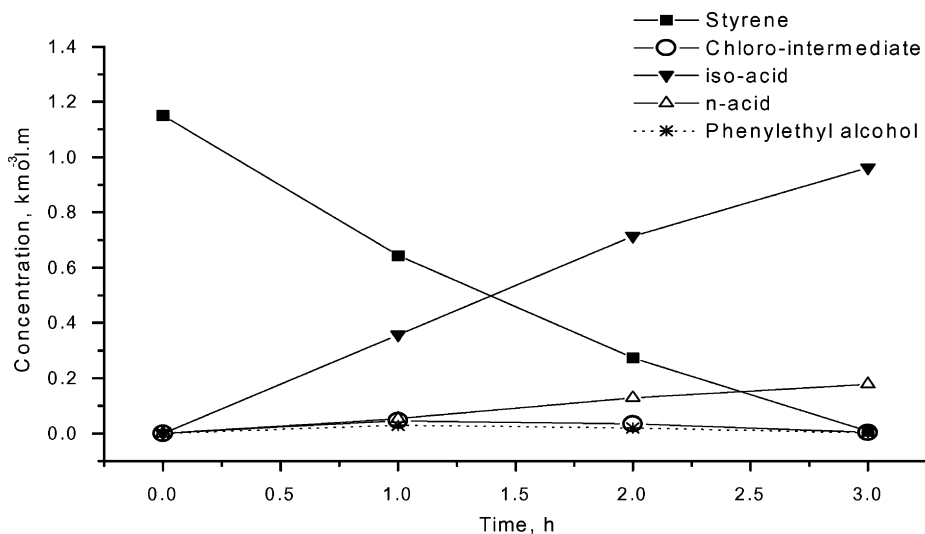


Fig. 1. A typical concentration–time profile for hydrocarboxylation of styrene using complex **2**/*p*-TsOH/LiCl under biphasic conditions. Reaction conditions: Pd, 0.0629 mmol; styrene, 28.8 mmol; *p*-TsOH, 11.2 mmol; LiCl, 11.2 mmol; H<sub>2</sub>O, 6 ml; toluene, 15.5 ml;  $P_{CO}$ , 5.4 MPa;  $T$ , 388 K.

thereby promoting the formation of the phenyl ethyl chloride, as well as the overall catalytic reaction.

### 3.3. Catalyst recycle experiments

It was important to check whether the catalyst was reusable after the reaction. For this purpose, a few recycle experiments were carried out after separating the aqueous catalyst from the organic (toluene) phase. The recycle of catalyst after a reaction at 388 K showed only very low catalytic activity ( $TOF = 25 \text{ h}^{-1}$ ) (Fig. 2a). However, at lower temperatures (373–378 K), the aqueous catalyst layer can be efficiently recycled giving consistent TOFs (Fig. 2b). In all these cases, analysis of Pd content by AAS in the organic phase after a reaction showed only <0.05–0.1 ppm of Pd, indicating negligible leaching of Pd to the organic phase. The catalyst was, however, efficiently reusable even at 388 K, when the recycle was carried out by adding fresh styrene to the reaction mixture under CO atmosphere,  $TOF = 269, 255 \text{ h}^{-1}$  for two successive recycles, respectively. The analysis of the organic layer for Pd content after two such recycles also showed only <0.1 ppm of Pd in the organic phase. These observations indicate that the catalyst is stable during experiment under CO atmosphere and

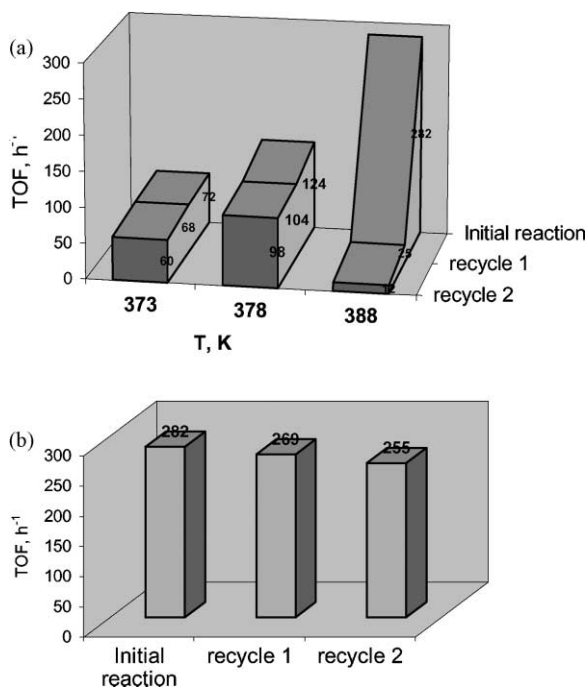


Fig. 2. Catalyst recycles: (a) after phase separation; (b) by adding fresh styrene to the reaction mixture under CO at 388 K.

efficient recycle of the catalyst can be achieved. High conversions (91%) achieved even at higher substrate concentrations (32%) also support this argument.

### 3.4. Effect of TPPTS/Pd ratio

The ratio of the water-soluble ligand, TPPTS to Pd ratio is known to have a significant effect on the performance of the catalyst in many biphasic catalytic reactions [9]. For example, an optimum of 4–6 equiv. of TPPTS to Pd was required to obtain the highest catalytic activity in PdCl<sub>2</sub>/TPPTS catalysed carbonylation of styrene [8]. But in the present catalytic system, maximum catalytic activity and selectivity to 2-arylpropanoic acid was achieved with 2 equiv. of TPPTS to Pd. Further increase in TPPTS concentration lowered the catalytic activity as well as 2-phenylpropionic acid selectivity significantly (Fig. 3). It is remarkable to mention that for our system, at 6 equiv. the desired parameters went down to a fifth of their respective values at 2 equiv. This may be due to the fact that at higher concentrations of TPPTS, the catalytic cycle may operate through the in situ formed Pd(TPPTS)<sub>3</sub> as the active catalyst, similar to the classical biphasic system of Sheldon and co workers [8].

### 3.5. Effect of styrene concentration

Reactions were carried out with different styrene concentrations to investigate the dependence of the reaction on styrene. The effect of styrene concentration on the TOF is shown in Fig. 4 for 388 K. It was observed that the catalytic activity increased steadily and linearly with styrene concentration, while the selectivity for the 2-phenylpropanoic acid was only marginally changed. The TOF increased with the increase in concentration of styrene up to 32% w/w concentration (57.7 mmol), presumably due to the increase in concentration of styrene in the aqueous catalytic phase in equilibrium with the organic phase.

### 3.6. Effect of CO partial pressure

Reactions were carried out with varying CO partial pressure keeping all other reaction parameters constant. The variation pattern is shown in Fig. 5. The catalytic activity was found to increase with the increase in the CO partial pressure up to a certain limit of ~4.0 MPa (conversion: 98.7%) and then remains almost constant on further increase (conversion: 99.0% at ~5.2 MPa). The selectivity to the 2-phenylpropanoic acid also follows a similar pattern.

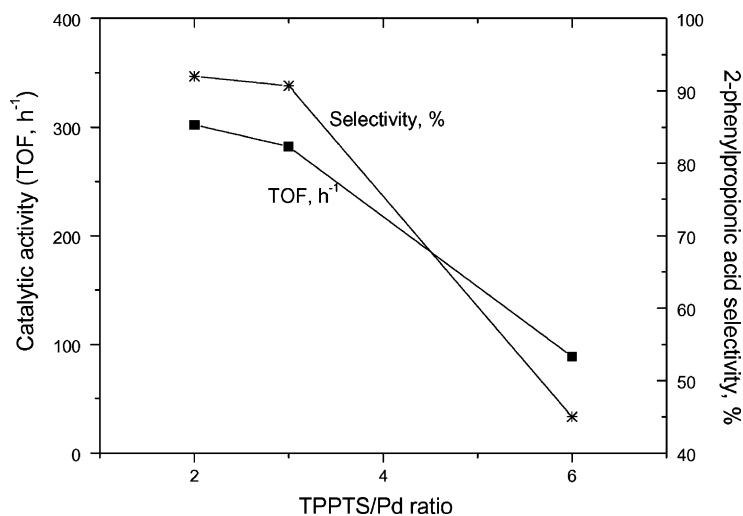


Fig. 3. Effect of Pd/TPPTS ratio on biphasic hydrocarboxylation of styrene. Reaction conditions: Pd, 0.0629 mmol; styrene, 28.8 mmol; *p*-TsOH, 11.2 mmol; LiCl, 11.2 mmol; H<sub>2</sub>O, 6 ml; toluene, 15.5 ml; *P*<sub>CO</sub>, 5.4 MPa; *T*, 388 K.

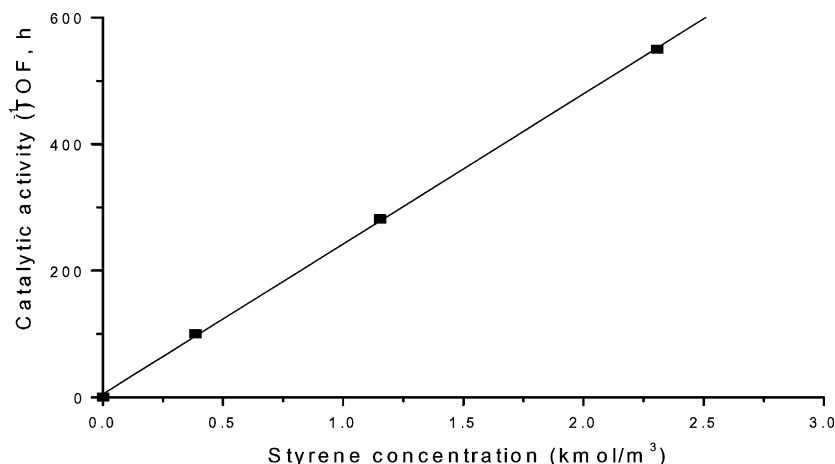


Fig. 4. Effect of concentration of styrene on biphasic hydrocarboxylation. Reaction conditions: Pd, 0.0629 mmol; TPPTS/Pd, 3; *p*-TsOH, 11.2 mmol; LiCl, 11.2 mmol; H<sub>2</sub>O, 6 ml; toluene, 15.5 ml; *P*<sub>CO</sub>, 5.4 MPa; *T*, 388 K.

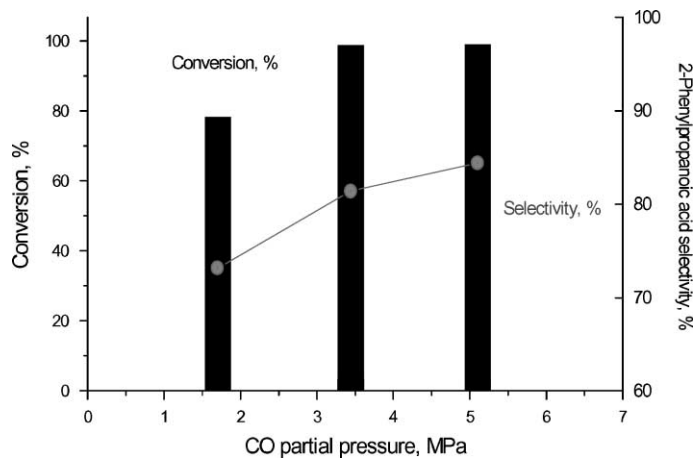


Fig. 5. Effect of CO partial pressure.

This variation might be due to the solubility limit of the gaseous carbon monoxide in the reaction medium under the reaction conditions.

### 3.7. Other substrates

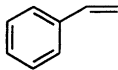
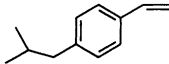
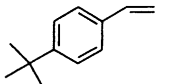
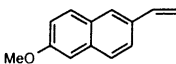
The catalytic system was found to be highly active and selective for the hydrocarboxylation of styrene, and hence it was applied to other vinyl aromatic compounds to investigate the catalytic activity and product selectivity for broadening the applicability. The various substrates used and the results obtained

are represented in Table 2. In general, high regioselectivity ( $\geq 93\%$ ) to all the 2-arylpropanoic acids was observed, but the highest catalytic activity was observed with styrene ( $\text{TOF} = 282 \text{ h}^{-1}$ ). This may, however, be consistent with the molecular steric factors guiding their coordination to the metal centre.

## 4. Reaction mechanism and catalytic cycle

As demonstrated before, in the case of hydrocarboxylation of vinyl aromatics using *p*-TsOH/LiCl

Table 2  
Hydrocarboxylation of different vinyl aromatic compounds<sup>a</sup>

Substrate	Time (h)	Conversion (%)	TOF (h <sup>-1</sup> )	Selectivity (%)	
				Iso	Linear
	1.5	91	282	95	8.7
	5	81	147	98	1.5
	3	90	273	96.6	2.8
	12	45.5	10	93	6.5

<sup>a</sup> Reaction conditions: Pd, 0.0629 mmol; TPPTS/Pd, 3; substrate, 28.8 mmol; *p*-TsOH, 11.2 mmol; LiCl, 11.2 mmol; H<sub>2</sub>O, 6 ml; toluene, 15.5 ml; *P*<sub>CO</sub>, 54 bar; *T*, 388 K.

promoters, the major active carbonylation substrate is the corresponding organic halide formed in situ under reaction conditions. Organic halides can be activated by oxidative addition either to a Pd(0) complex forming Pd(II) alkyl complex [1,14] or to a highly nucleophilic Pd(II) complex forming a Pd(IV) alkyl complex [2,15,16] which may undergo further CO insertion and reductive elimination steps to form the product acids. In order to understand the nature of Pd species formed in solution under reaction conditions, a few <sup>31</sup>P NMR experiments were carried and the results are discussed below.

An aqueous solution of Pd complex **2** obtained after exchange of PPh<sub>3</sub> of complex **1** in the presence of 3 equiv. of TPPTS (at room temperature) showed two broad <sup>31</sup>P NMR signals centred at 36.26 and 35.27 ppm in addition to a strong sharp signal at 32.50 ppm and a few weak signals at 30.91, 29.22 and 20.14 ppm (Fig. 6). The signal of free TPPTS was observed at -4.14 with a downfield shift of 0.8 ppm from that of an aqueous solution of free TPPTS. The broad signals are indicative of equilibrium between two species or with free TPPTS. The complex **2** isolated showed two strong signals at 36.13 ppm (slightly broad) and 35.31 ppm (sharp) along with some weak signals at 31.61, 31.30, 30.47, 29.45, 23.88 and 23.11 ppm. No signals of free TPPTS was observed in this case. The strong signals at 35.31 and 36.13 ppm in the isolated complex are assigned to **2** and **2'**, respectively. The isomer **2** being stabler

(trans-effect and steric factors play part) gives a sharp peak, while the complex **2'** may have some equilibrium fluctuation between similar other species formed in situ, producing the broadening. The identification of these was not possible by low temperature NMR experiments as the solvent (water) starts freezing. In the presence of excess TPPTS, complexes of the type **3** and **4** can also be formed. The signal at 32.50 ppm can be due to **3** or **4**, since it was observed only in the presence of free TPPTS in solution (Scheme 3).

In the presence of *p*-TsOH and LiCl (same concentrations as that under reaction conditions), the <sup>31</sup>P NMR spectrum was entirely different (Fig. 7). In this case, the signals at 36.26, 35.27, 30.91, 29.22 and 20.14 ppm disappeared with slight decrease in the intensity of the signal at 32.50 ppm. Two new sharp signals at 34.93 and 26.14 ppm appeared in addition to the signal corresponding to free TPPTS. The signal at 34.93 ppm corresponds to oxide of TPPTS (TPPTSO) in comparison with a standard aqueous sample (34.9 ppm). The formation of TPPTSO in this sample indicates a probable formation of a Pd(0) species. Hence, the signal at 26.14 ppm was assigned to a Pd(0) species of type **5** (Scheme 4) by considering the fact that Pd(0) species formed in the presence of halide ions are solvated with halide ions to form the corresponding anionic Pd(0) complexes.

The same reaction was repeated in the presence of either *p*-TsOH or LiCl alone. In the presence of only LiCl, the major signal observed was at 22.51 ppm,



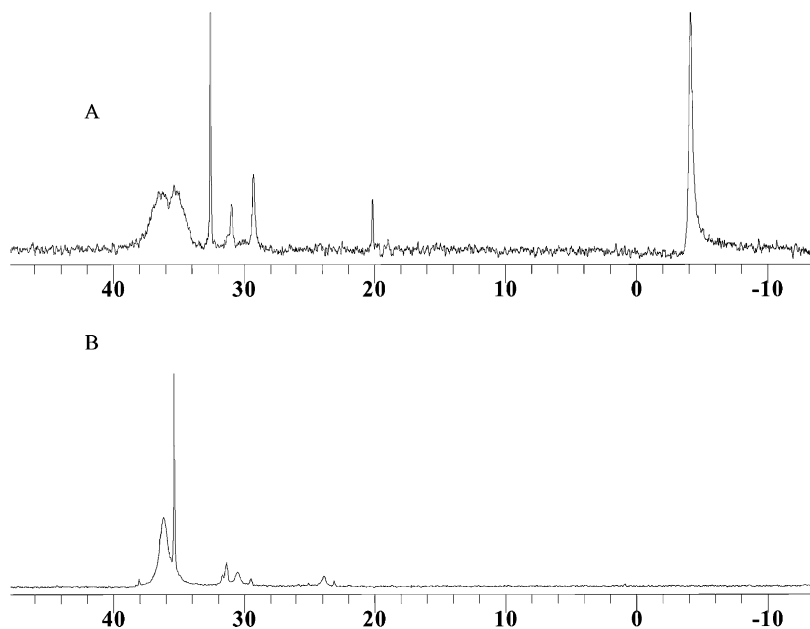
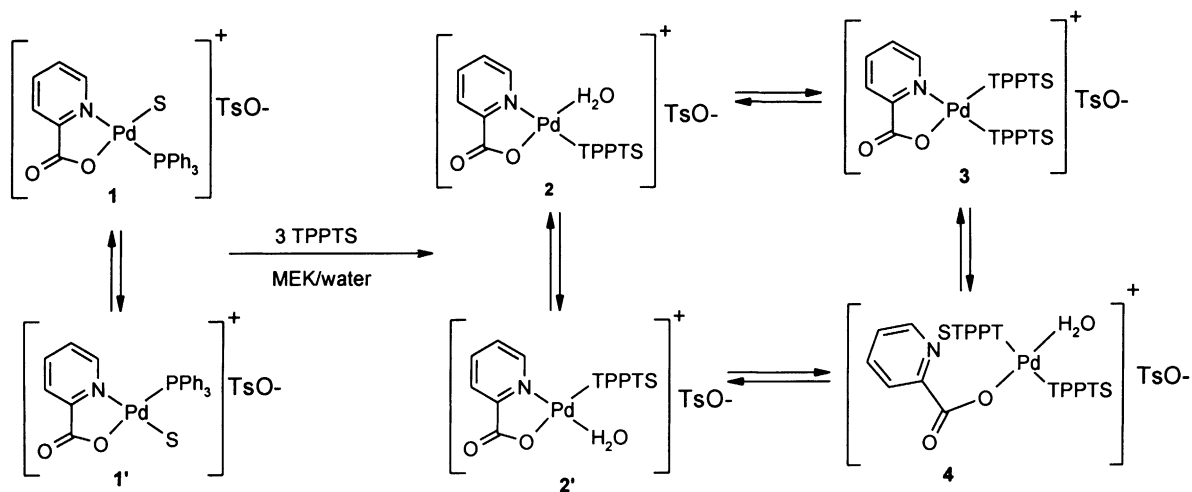


Fig. 6.  $^{31}\text{P}$  NMR spectrum: (A) in aqueous yellow solution obtained after exchange of  $\text{PPh}_3$  of complex **1** in the presence of 3 equiv. of TPPTS at room temperature; (B) complex **2** after isolation.

which can be assigned to a di-anionic  $\text{Pd}(0)$  complex of the type  $[\text{Pd}^0(\text{TPPTS})_2\text{Cl}_2]^{2-}(\text{Li}^+)_2$  in comparison with the reported  $^{31}\text{P}$  NMR chemical shift values (23.15 ppm) of a similar species  $[\text{Pd}^0(\text{PPh}_3)_2\text{Cl}_2]^{2-}$  [3,17]. Only in the presence of *p*-TsOH, the  $^{31}\text{P}$  NMR spectrum was too complex.

For a comparison, similar reactions were carried out using a mixture of  $\text{PdCl}_2$  and 4 equiv. of TPPTS. A mixture of  $\text{PdCl}_2$  and 4 equiv. of TPPTS in water after 15–30 min of stirring formed a yellow solution  $^{31}\text{P}$  NMR, which showed a doublet at 31.53 ppm and a triplet at 34.792 ppm ( $J = 14.88$  Hz) (Fig. 8). These



Scheme 3. Various types of possible Pd species.

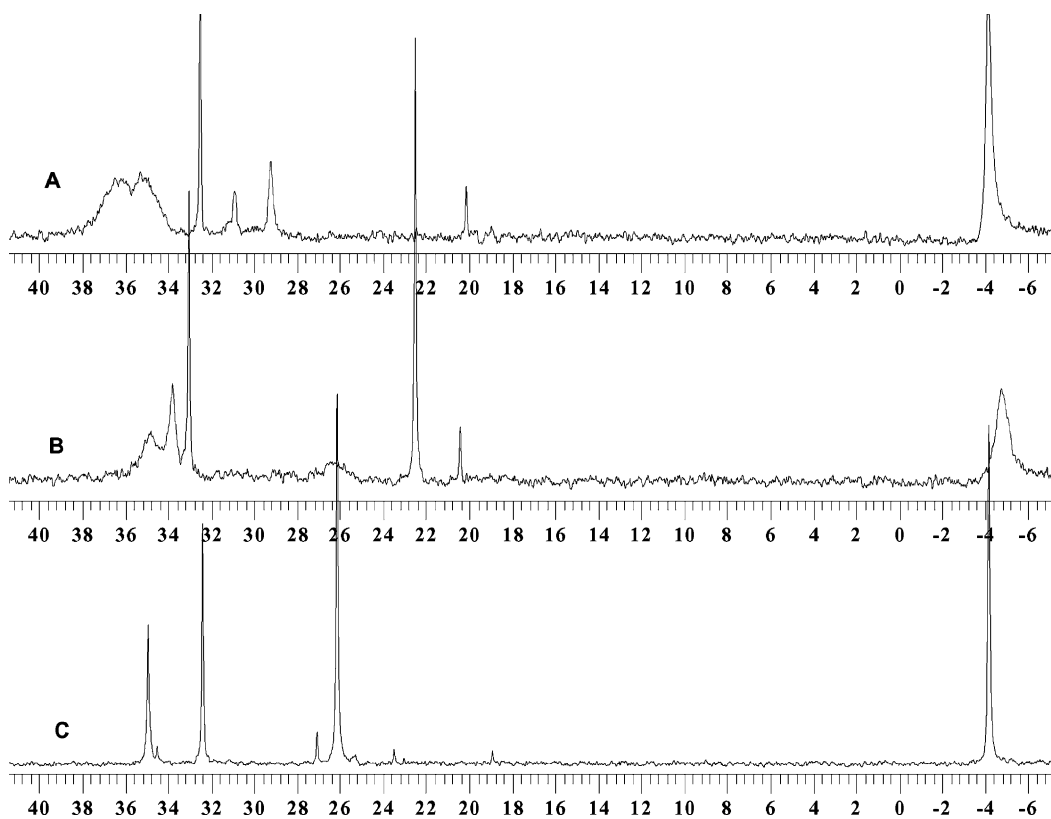
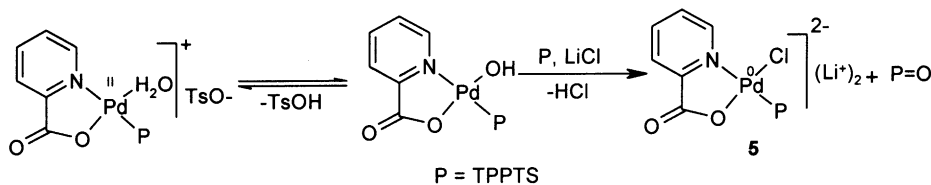


Fig. 7.  $^{31}\text{P}$  NMR spectrum: (A) in aqueous yellow solution obtained after exchange of  $\text{PPh}_3$  of complex **1** in the presence of 3 equiv. of TPPTS; (B) in the presence of only LiCl; (C) in the presence of *p*-TsOH and LiCl.

signals correspond to the complex  $[\text{Pd}(\text{TPPTS})_3\text{Cl}]^+$  [4]. In addition, two sharp singlets at 35.26 and 36.16 ppm were also observed in this case. The signal at 35.26 ppm can be assigned to  $\text{PdCl}_2(\text{TPPTS})_2$  in comparison with the literature reported values [5]. The signal at 36.16 ppm may be due to di-cationic complexes of the type  $[\text{Pd}(\text{TPPTS})_3]^{2+}$ . No free TPPTS was observed in this sample.

When *p*-TsOH and LiCl were added to this solution, the signals at 31.53(d) and 34.79(t) ppm disappeared with the development of strong signals at 33.95 and 35.60 ppm. In this case, a small broad signal at 25.71 ppm was also observed, which can be assigned to  $[\text{Pd}(\text{TPPTS})_3\text{Cl}]^-$  in comparison with the literature values of analogous complexes with  $\text{PPh}_3$  as the ligand such as  $[\text{Pd}(\text{PPh}_3)_3\text{Cl}]^-$  (25.22 ppm) [6,18].



Scheme 4. Formation of Pd(0) species.

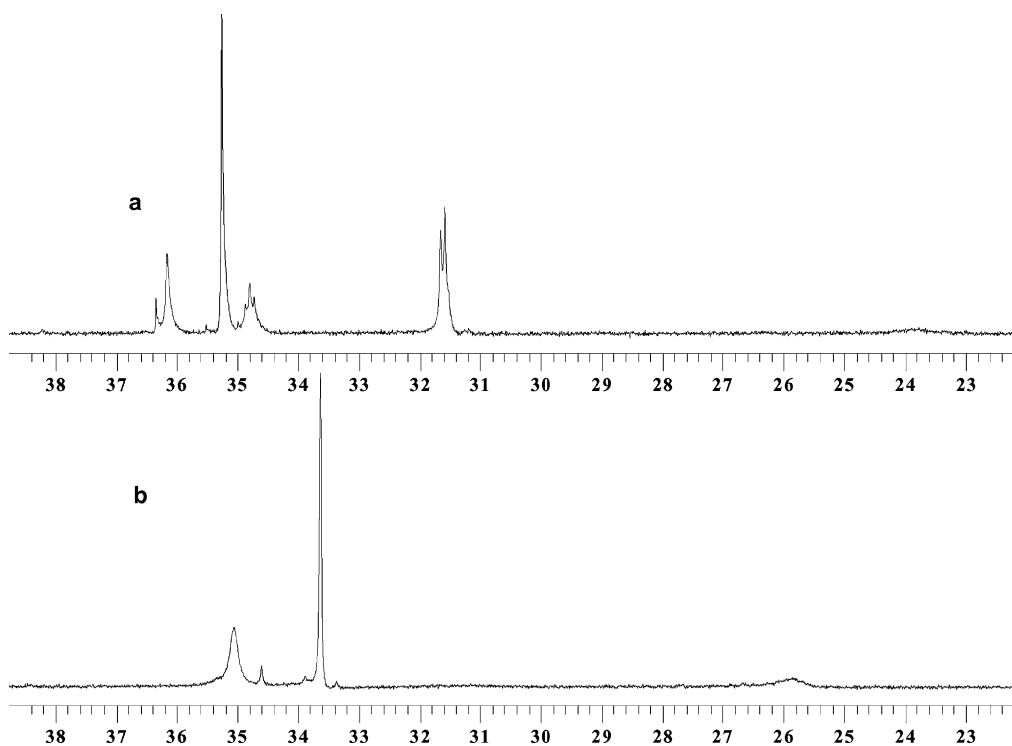


Fig. 8.  $^{31}\text{P}$  NMR spectrum: (a) in aqueous solution of a mixture of  $\text{PdCl}_2/4$  equiv. of TPPTS; (b) in the presence of *p*-TsOH and LiCl at room temperature.

In an atmosphere of CO, whether bubbled or under pressure, the colour of both the catalyst precursor systems was found to immediately change from yellow to orange, which on exposure to air changes back to yellow. This observation indicates CO coordination occurs immediately after the catalyst precursors come in contact with CO. In the presence of CO, both these catalytic systems showed a similar  $^{31}\text{P}$  NMR pattern with small shift in the signals. Thus, the  $^{31}\text{P}$  NMR spectrum of an aqueous solution of  $\text{PdCl}_2/4$  equiv. of TPPTS in the presence of *p*-TsOH and LiCl after reaction with CO under 2.1 MPa at 348 K for 15 min showed a sharp signal at 34.37 ppm and a broad signal centred at 22.91 ppm (Fig. 9). The signal at 22.91 ppm can be assigned to  $\text{Pd}^0(\text{TPPTS})_3$  [4], in equilibrium with Pd(0) carbonyl complexes of the type  $\text{Pd}(\text{TPPTS})_n(\text{CO})_m$ . The sharp signal at 34.37 ppm may be due to some neutral or cationic Pd(II) or anionic Pd(0) complexes such as  $\text{Pd}^{\text{II}}(\text{TPPTS})_2\text{Cl}_2$ ,  $[\text{Pd}^{\text{II}}(\text{TPPTS})_2(\text{CO})\text{Cl}]^+$ , and

$[\text{Pd}^0(\text{TPPTS})_2(\text{CO})\text{Cl}]^-$ . No signal corresponding to free TPPTS was observed in this case.

The yellow aqueous solution of Pd complex **2** obtained after exchange of  $\text{PPh}_3$  of **1** in the presence of 3 equiv. of TPPTS also showed immediate colour changes to orange after reaction with CO under 2.1 MPa at 348 K for 15 min. The  $^{31}\text{P}$  NMR spectrum of this sample showed two strong broad signals at 34.63 (with a shoulder at 35.49 ppm) and 24.24 ppm. In this case also the signal at 22.9 ppm was observed, but was very weak. When the same reaction was carried out in the presence of *p*-TsOH and LiCl, a new signal at 23.57 ppm was developed in addition to other signals. The signal at 24.24 ppm in this case was found to be very broad, which indicates two or more species in equilibrium or complexes having fluxional behaviour. Thus the signals between 23 and 25 ppm are assigned to neutral or anionic Pd(0) carbonyl complexes with Pyca as one of the ligands as shown in Scheme 5.

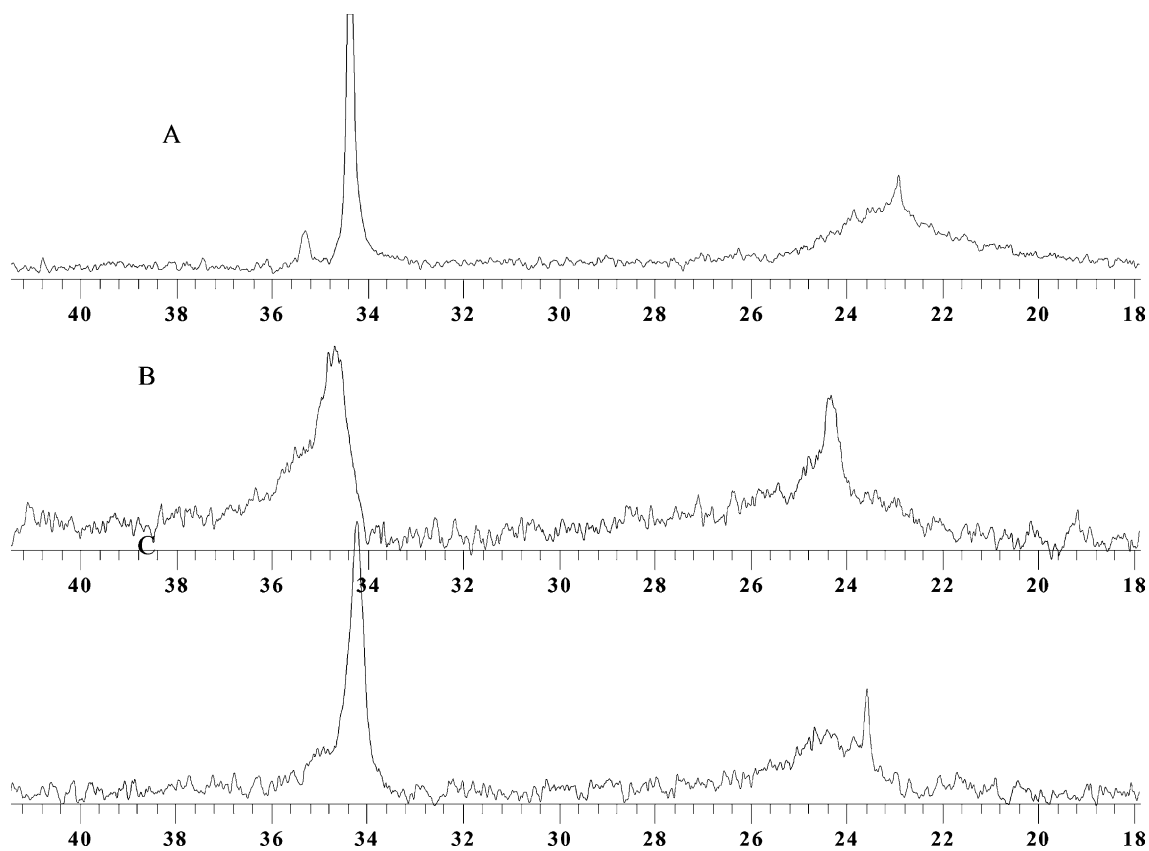
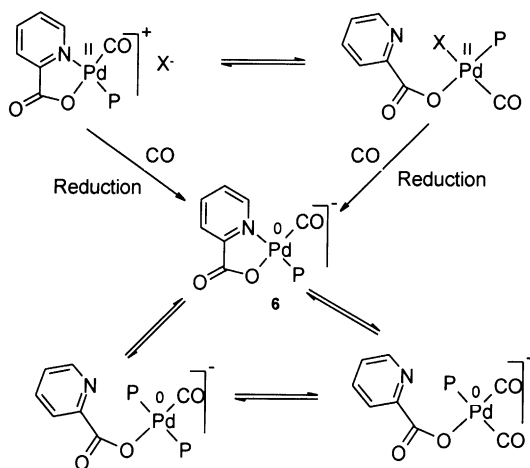
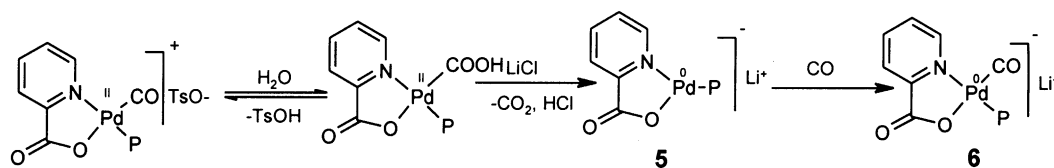


Fig. 9.  $^{31}\text{P}$  NMR spectrum: (A)  $\text{PdCl}_2/4$  equiv. of TPPTS/*p*-TsOH/LiCl under CO; (B) complex 2 under CO; (C) complex 2/*p*-TsOH/LiCl under CO.



Scheme 5. Different types of Pd(II) and Pd(0) species which may be formed under reaction conditions.



Scheme 6. Formation of Pd(0) species under CO.

The reduction of Pd(II) species to Pd(0) species can also take place through a kind of water-gas shift reaction in the presence of CO and H<sub>2</sub>O as shown in Scheme 6.

The apparent difference in catalytic activity between **2** and PdCl<sub>2</sub>/TPPTS as the catalyst precursors indicates that the active catalytic species formed may be different in both the cases. This is also supported by the difference in <sup>31</sup>P NMR signals observed after the reaction of both the catalytic systems with CO.

In order to understand the nature of active catalytic intermediates formed during a carbonylation reaction, intermediate samples were withdrawn from the reaction mixture (using **2** as the catalyst) and

analysed immediately by <sup>31</sup>P NMR. In these samples, a new strong signal at 27.69 ppm and a weak signal at 18.85 ppm were observed along with the signals at 24.71 and 22.67 ppm (Fig. 10).

The signals at 24.71 and 22.67 ppm correspond to anionic or neutral Pd(0) species with or without Pyca, respectively, as described above. The signals at 27.69 and 18.85 ppm were tentatively assigned as Pd-alkyl (**7** or **8**, Scheme 7) and Pd-acyl (**9**, Scheme 7) species in comparison with literature values for similar species [7]. Based on these observations, a plausible catalytic cycle has been proposed (Scheme 7), which involves an anionic Pd(0) carbonyl complex **6** as the active species.

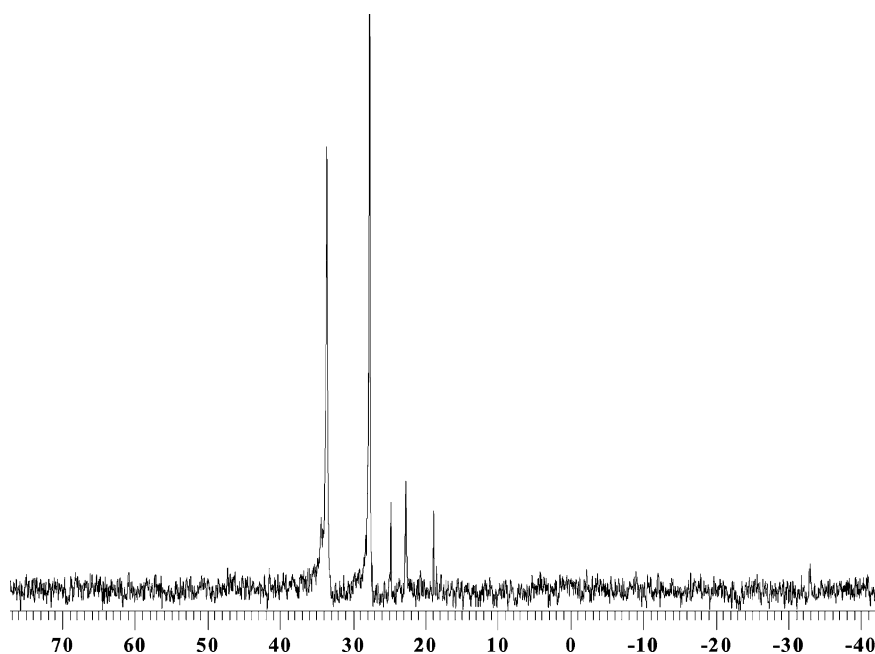
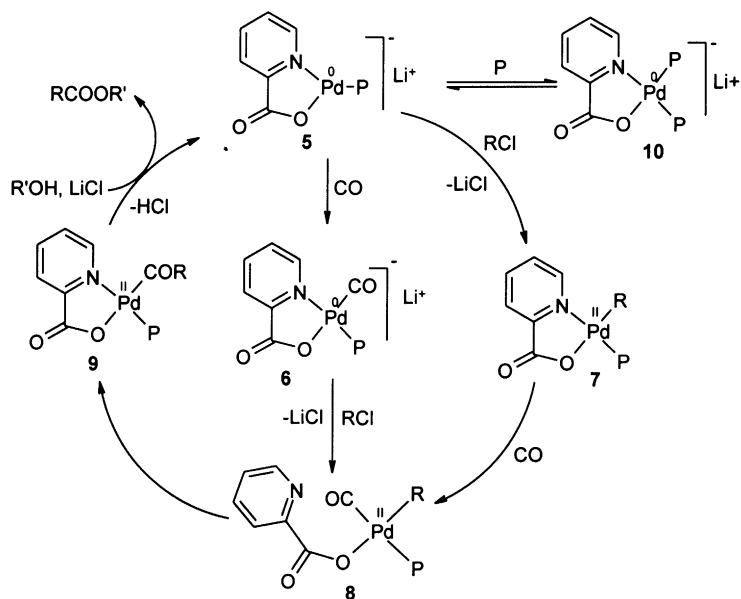


Fig. 10. <sup>31</sup>P NMR spectrum of intermediate sample from a biphasic carbonylation reaction using complex **2**/*p*-TsOH/LiCl as the catalyst system.



Scheme 7. Proposed catalytic cycle.

## 5. Conclusions

In this endeavour, we have shown that the biphasic catalytic system using the water-soluble palladium complex catalyst in the presence of a Brønsted acid and halide promoters is an efficient one for the hydrocarboxylation of vinyl aromatic compounds. The use of optimum conditions as visualized here leads to a very high activity and selectivity to the desired 2-arylpropanoic acids by carbonylation of vinyl aromatic compounds. The use of a lower amount of palladium in the catalytic system than the classical one, and further consistency in the negligible leaching of the same in the product mixture makes the system more effective. While studying the mechanistic details of the hydrocarboxylation reaction, it was shown that the reaction proceeds through the formation of a Pd(0) moiety which is supposed to be the active catalytic species, as suggested by the  $^{31}\text{P}$  NMR experiments. However, the substrate is converted to a halo-intermediate in the presence of the halide promoters under the reaction conditions, which acts as the active substrate. This study thus commits a new and better system for the carbonylation of vinyl aromatic compounds under milder conditions than the existing

ones with the facility of convenient separation of the products and recyclability of the catalyst.

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