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Catalytic conversions in water, part 8: carbonylation and hydrocarboxylation reactions catalyzed by palladium trisulfonated triphenylphosphine complexes[1]

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Abstract

The water-soluble $Pd(tppts)_3$ complex (tppts=$P(C_6H_4$-m-$SO_3Na)_3$) is an active catalyst for the carbonylation of benzylic type alcohols in aqueous/organic two-phase systems in the presence of a Brønsted acid cocatalyst. For example, 1-(4-isobutylphenyl)ethanol afforded 2-(4-isobutylphenyl)propionic acid in 82% selectivity at 83% conversion and 5-hydroxymethylfurfural (HMF) gave 5-formylfuran-2-acetic acid in 72% selectivity at 90% conversion. In the latter case, use of an acid with a strongly coordinating anion led to the preferential formation of the reduction product 5-methylfurfural (MF), e.g. HI afforded MF in >99% selectivity. $Pd(tppts)_3$ is also an usual active catalyst (T.O.F.>2500) for the biphasic hydrocarboxylation of propene to n- and isobutyric acid, being substantially more active than the analogous Pd/PPh_3 in organic media.

1. Introduction

Because of the broad range of potential applications there is a growing interest in organometallic catalysis in aqueous media [1]. The use of water circumvents the need for organic solvents and facilitates recovery and recycling of the catalyst which can provide for substantial environmental benefits.

Palladium catalyzes a variety of reactions such as carbonylations, hydrogenations, oxidations, C–C-coupling reactions, etc. [2]. Its potential in aqueous phase catalysis, however, is rather unexplored. In this paper we report our investigations of water-soluble palladium complexes of trisulfonated triphenylphosphine (tppts; $P(C_4H_6$-*m*-$SO_3Na)_3$) as catalysts for the carbonylation of benzylic alcohols and the hydrocarboxylation of olefins in aqueous media.

2. Synthesis of the $Pd(tppts)_3$-catalyst

A number of methods for the preparation of the homoleptic $Pd(tppts)_3$ complex have been described. For example, Herrmann et al. [3] prepared $Pd(tppts)_3$ in 52% yield by ligand exchange of $Pd(PPh_3)_4$ with tppts in a toluene/water mixture. This procedure leads to moderate yields and requires a large excess of tppts and rather expensive palladium starting material. Moreover, the product can be contaminated with the low-ligated zerovalent $Pd(tppts)_2$ complex.

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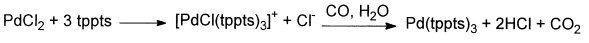
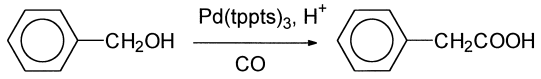


Scheme 1. The preparation of $Pd(tppts)_3$ by reduction of $[PdCl(tppts)_3]^+$ with carbon monoxide.



Scheme 2. The carbonylation of benzyl alcohol catalyzed with $Pd(tppts)_3$.

$Pd(tppts)_3$ is also obtained by reduction of K_2PdCl_4 with $NaBH_4$ in the presence of tppts. This route requires expensive reducing agents and yields products contaminated with inorganic salts and unreacted potassium tetrachloropalladate(II), which necessitates a cumbersome purification by gelpermeation chromatography.

Using ^{17}O-, ^{31}P- and ^{35}Cl-NMR we showed that the $[PdCl(tppts)_3]^+$ intermediate is formed quantitatively from $PdCl_2$ and tppts in water and that this cationic complex is reduced to $Pd(tppts)_3$ by tppts itself [4]. However, the reduction takes 8 days to go to completion and the concomitant formation of one equivalent of tppts-oxide is disadvantageous. Subsequently we developed a simpler, more convenient route, which utilizes carbon monoxide to reduce the $[PdCl(tppts)_3]^+$ intermediate (Scheme 1).

$Pd(tppts)_3$ was obtained quantitatively (based on $PdCl_2$, tppts/Pd=6) within 5 min at 25°C under a carbon monoxide pressure of only 2 bar. The complex could be separated from the two equivalents of HCl by gelpermeation chromatography and it was obtained as a brownish yellow powder in 100% yield.

Since this purification method is laborious, the catalyst used in all of the following carbonylation and hydrocarboxylation reactions was synthesized in situ after complexation of $PdCl_2$ with tppts in H_2O and subjection of the formed $[PdCl(tppts)_3]^+$ to a carbon monoxide atmosphere under the chosen carbonylation reaction conditions.

3. The carbonylation of benzyl alcohol

Activated benzyl alcohols such as 4-hydroxybenzyl alcohol are carbonylated to 4-hydroxyphenylacetic acid ethyl ester in the presence of classical hydrophobic Pd/PPh_3 catalysts in organic solvents (ethanol). However, benzyl alcohol itself is unreactive [5].

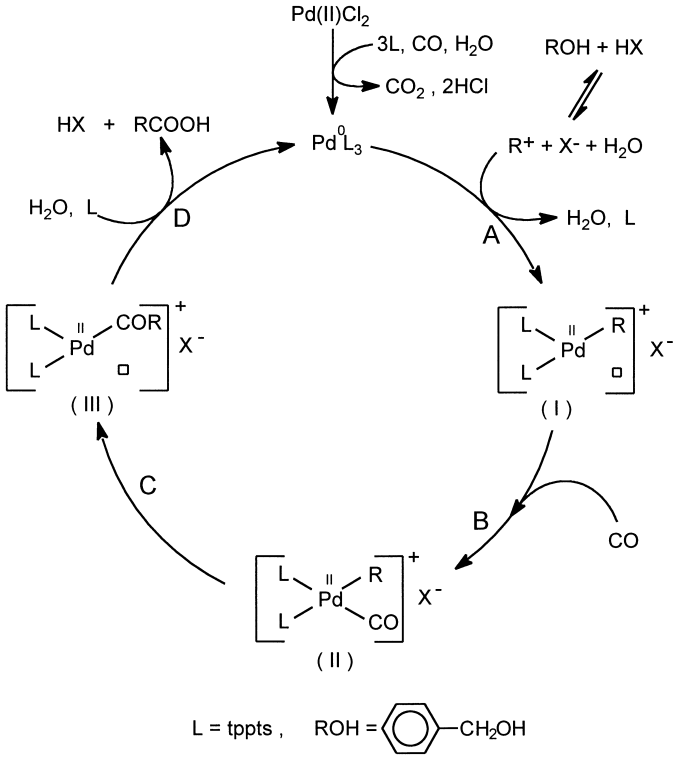
We found that $Pd(tppts)_3$ is an effective catalyst for the carbonylation of benzyl alcohol to phenylacetic acid (Scheme 2) under mild reaction conditions in an acidic aqueous medium [6]. The only product obtained was phenylacetic acid without any formation of toluene (the reduction product) or the dibenzyl ether. The best result (77% yield of phenylacetic acid, ≈100% selectivity) was obtained at 100°C and a tppts/Pd molar ratio of 12 (Table 1).

Table 1
The carbonylation of benzyl alcohol to phenylacetic acid with $Pd(tppts)_3$

Run [a]	Temperature (°C)	P/Pd molar ratio	Yield (%) Phenylacetic acid
1/1	70	10	7
1/2	80	10	18
1/3	90	10	29
1/4	100	10	49
1/5	110	10	36
1/6	100	6	42
1/7	100	8	45
1/8	100	12	77

[a] Reaction conditions: 35.5 mg (0.2 mmol) $PdCl_2$, tppts, 541 mg (5 mmol) benzyl alcohol [benzyl alcohol/Pd=25], 1.902 g (10 mmol) p-$CH_3C_6H_4SO_3H$ [H^+/benzyl alcohol=2], addition of deaerated H_2O for 141.9 g of reaction mixture, [Pd]=150 ppm P_{CO}: 60 bar, t: 10 h.

We propose the catalytic cycle, depicted in Scheme 3, to explain the observed $Pd(tppts)_3$-catalyzed carbonylation of benzyl alcohol. A benzylpalladium(II) intermediate (I) is formed by an oxidative addition of the benzylic carbenium ion, formed by reaction of benzyl alcohol with the Brønsted acid, to $Pd(tppts)_3$. Coordination of CO at the free coordination site of intermediate I and subsequent migratory insertion of carbon monoxide into the palladium alkylbond results in the cationic acyl species (III). Finally, nucleophilic attack of H_2O on the acyl carbon in intermediate (III) gives phenylacetic acid and, after coordination of tppts, the catalyst returns to the catalytic cycle. The vacant coordination sites in intermediate I and III, can temporarily be occupied by the ligand, the anion or solvent molecules.



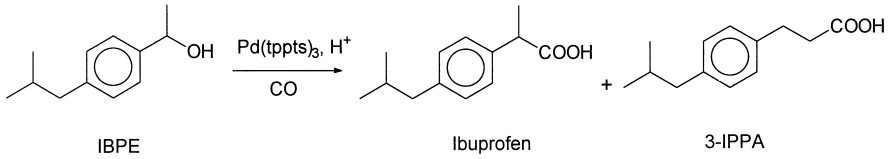
Scheme 3. Proposed mechanism for the carbonylation of benzyl alcohol catalyzed by $Pd(tppts)_3$.

4. The carbonylation of 1-(4-isobutylphenyl)ethanol (IBPE)

2-(4-isobutylphenyl)propionic acid, more commonly known as ibuprofen, is a nonsteroidal antiinflammatory drug with annual sales of approximately $ 1400 million and a production volume of 8000 tpa [7]. Hoechst Celanese Corporation in cooperation with the Boots company developed an attractive route for the synthesis of ibuprofen. In this BHC Ibuprofen process 1-(4-isobutylphenyl)ethanol (IBPE) is carbonylated in the presence of a Pd/PPh_3 catalyst in organic media. The conversion of IBPE is 99% and the selectivity to ibuprofen is 96%. A shortcoming of this process is the cumbersome separation of the catalyst from reaction products and its quantitative recovery in an active form. In the manufacture of pharmaceuticals the quantitative separation of the catalyst is even more important in order to avoid contamination of the product by trace amounts of heavy metals, which could necessitate extensive purification. Therefore we studied the carbonylation of IBPE with water-soluble palladium complexes in an aqueous/organic two phase system [8].

No organic solvent was used since only traces of products were obtained when toluene was added. Apparently this leads to an unfavorable distribution of IBPE between the organic and aqueous phase. In addition to ibuprofen, its linear isomer 3-(4-isobutylphenyl)propionic acid (3-IPPA) and trace amounts of the dehydration product, isobutylstyrene (IBS) were formed (Scheme 4). The highest yield of ibuprofen was obtained with tppts/Pd=10 (Table 2). Further increase of the ligand/Pd ratio led to a slight decrease in the activity of the catalyst, accompanied by a slight increase in selectivity to ibuprofen (63% at tppts/Pd=12). In the absence of tppts only IBS was obtained.

The $Pd(tppts)_3$-catalyzed carbonylation of IBPE is strongly influenced by the addition of a Brønsted acid. The rate increases with increasing amounts of *p*-toluenesulfonic acid (Table 3). A maximum turnover



Scheme 4. The carbonylation of IBPE catalyzed by $Pd(tppts)_3$.

Table 2
The carbonylation of IBPE to ibuprofen with $Pd(tppts)_3$ at different P/Pd molar ratios

Run [a]	P/Pd molar ratio	Conversion [b] (mol%)	Selectivity [b] (mol%)		
			Ibuprofen	3-IPPA	IBS
2/1	0	12	tr	tr	99
2/2	6	32	53	47	tr
2/3	8	46	55	45	tr
2/4	10	58	59	41	tr
2/5	12	52	63	37	tr

[a] Reaction conditions: 35.5 mg (0.2 mmol) of $PdCl_2$ tppts, 891.4 mg (5 mmol) of IBPE [IBPE/Pd=25]; 1.617 g (8.5 mmol) of p-$CH_3C_6H_4SO_3H$[H^+/IBPE=1.7]; addition of deaerated distilled H_2O for 141.9 g of aqueous reaction mixture; [Pd]=150 ppm, T: 70°C; P_{CO}: 50 bar; t: 10 h.
[b] Determined by HPLC on the basis of IBPE.

frequency (TOF, mol of converted IBPE/mol Pd·h) of 2.3 h^{-1} was observed at H^+/IBPE=2.

Using acids with weakly or non coordinating anions, such as p-toluenesulfonic, trifluoroacetic or hexafluorophosphoric acid, ibuprofen was obtained with selectivities of 67–77%. In sharp contrast, no catalytic activity was observed with acids of strongly coordinating anions such as hydrogen iodide.

The effect of temperature and the CO pressure is shown in Table 4. The optimum result (82% selectivity at 83% conversion) was obtained at 90°C. Nevertheless, the catalyst appears to be most stable at 70°C since at this temperature no metallic palladium was formed and the aqueous phase remained a clear yellow solution. The selectivity to ibuprofen was strongly influenced by the temperature and the CO pressure. High selectivities were obtained at a high CO pressure (150 bar) and a low reaction temperature. The selectivity decreased significantly with decreasing CO pressure and when the temperature was raised.

We suggest that the formation of ibuprofen proceeds via the same mechanism as that shown for benzyl alcohol (Scheme 3). Isomerization of the palladium-alkyl intermediate (IA) via β-hydride elimination and re-insertion of the olefin in the Pd–H bond leads to the formation of the linear isomer of ibuprofen, 3-IPPA (Scheme 5).

Table 3
The carbonylation of IBPE to ibuprofen catalyzed by $Pd(tppts)_3$. Addition of different Brønsted acids

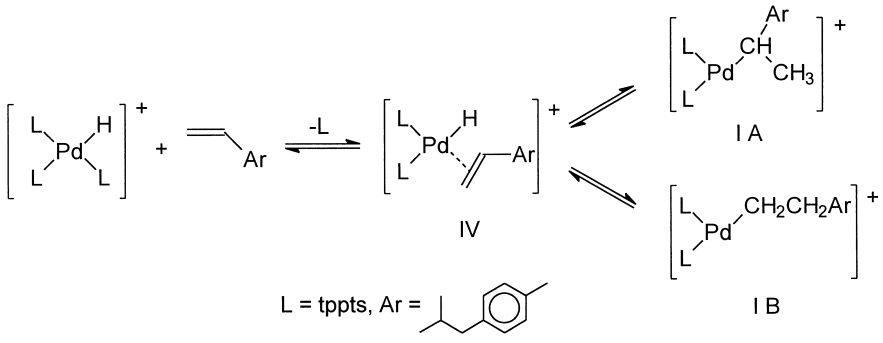
Run [a]	Acid added	(mmol)	Conversion (mol%)	Selectivity [b] (mol%)		
				Ibuprofen	3-IPPA	IBS
3/1	p-$CH_3C_6H_4SO_3H$	(4.0)	53	75	25	tr
3/2	p-$CH_3C_6H_4SO_3H$	(6.0)	71	73	27	tr
3/3	p-$CH_3C_6H_4SO_3H$	(8.0)	85	72	28	tr
3/4	p-$CH_3C_6H_4SO_3H$	(10.0)	93	72	28	tr
3/5	p-$CH_3C_6H_4SO_3H$	(12.0)	86	71	29	tr
3/6 [b]	p-$CH_3C_6H_4SO_3H$	(8.50)	58	59	41	tr
3/7 [b]	CF_3COOH	(8.50)	55	67	33	tr
3/8 [b]	HPF_6	(8.50)	53	77	23	tr
3/9 [b]	HCl	(8.50)	48	71	29	tr
3/10 [b]	H_2SO_4	(4.25)	44	68	32	tr
3/11 [b]	HI	(8.50)	11	tr	tr	99

[a] Reaction conditions: 35.5 mg (0.2 mmol) of $PdCl_2$; 1136.3 mg (2 mmol) of tppts [P/Pd=10]; 891.4 mg (5 mmol) of IBPE [IBPE/Pd=25]; addition of deaerated distilled H_2O for 141.9 g of aqueous solution; [Pd]=150 ppm; T: 90°C; P_{CO}: 60 bar; t: 10 h.
[b] P_{CO}: 50 bar

Table 4
The carbonylation of IBPE to ibuprofen catalyzed by $Pd(tppts)_3$ at different temperatures and carbon monoxide pressures

Run [a]	*p*-$CH_3C_4H_6SO_3H$ (mmol)	Temperature (°C)	CO pressure (bar)	*t* (h)	Conversion (mol%)	Selectivity (mol%)		
						Ibuprofen	3-IPPA	IBS
4/1	1.0	70	30	20	11	72	27	tr
4/2 [b]	1.0	80	30	20	36	69	30	tr
4/3 [b]	1.0	90	30	20	49	62	38	tr
4/4 [b]	1.0	100	30	20	44	55	45	tr
4/5	4.0	90	150	10	83	82	18	tr
4/6	4.0	90	100	10	83	80	20	tr
4/7	4.0	90	60	10	84	70	29	tr
4/8	4.0	90	30	10	86	68	32	tr
4/9 [b]	4.0	90	5	10	87	54	46	tr

[a] Reaction conditions: 35.5 mg (0.2 mmol) of $PdCl_2$; 1136.3 mg (2 mmol) of tppts [P/Pd=10]; 445.7 mg (2.5 mmol) of IBPE [IBPE/Pd=12.5]; addition of deaerated distilled H_2O for 141.9 g of aqueous solution, [Pd]=150 ppm.
[b] Formation of metallic Pd.



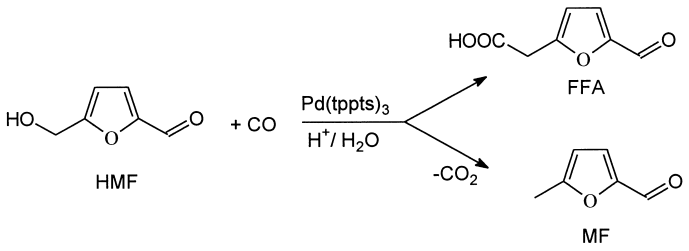
Scheme 5. Reaction of IBS with the cationic palladium hydride.

Alternatively, both carboxylic acids can be formed via acid catalyzed dehydration of IBPE to IBS, followed by Pd/tppts catalyzed hydrocarboxylation (vide infra).

5. The carbonylation of 5-hydroxymethylfurfural (HMF)

Interest in the use of carbohydrates as renewable raw materials is increasing, stimulated both by the projected long-term scarcity of fossil feedstocks and by environmental restrictions regarding the biodegradability and biocompatibility of many petrochemical-based products [9]. 5-Hydroxymethylfurfural (HMF) is readily obtained from acid-catalyzed dehydration of various carbohydrates, especially fructose [9], [10]. Because it contains both an aldehyde and a primary alcohol functionality HMF constitutes a relatively simple model compound for carbohydrates. The highly hydrophilic nature of HMF means that water is the preferred solvent for reactions. Since $Pd(tppts)_3$ proved to be an excellent catalyst for the carbonylation of benzylic alcohols (vide supra), we reasoned that it should also catalyze facile carbonylation of the quasi-benzylic alcohol, HMF. Indeed, we found that $Pd(tppts)_3$ catalyzed the carbonylation of HMF (Scheme 6) to afford 5-formyl furan-2-acetic acid (FFA) in a completely aqueous medium [6].

The only by-product observed was 5-methylfurfural (MF); no carbonylation of the aldehyde or *cis*-diene group of HMF was observed. The best yields of FFA were obtained under relatively mild conditions (70°C and 5 bar CO). The reaction is strongly influenced by



Scheme 6. $Pd(tppts)_3$ catalyzed carbonylation and reduction of HMF.

Table 5
The carbonylation and reduction of HMF with $Pd(tppts)_3$ at different P/Pd molar ratios

Run [a]	P/Pd molar ratio	Conversion [c] (mol %)	Selectivity [c] (%)	
			FFA	MF
5/1	0	0	0	
5/2	2	1	22	77
5/3	4	53	65	34
5/4	5	74	68	32
5/5	6	90	72	28
5/6 [b]	7	87	72	28
5/7 [b]	8	71	72	27
5/8 [b]	12	40	73	26

[a] Reaction conditions: 35.5 mg (0.2 mmol) $PdCl_2$, tppts, 0.63 g (5 mmol) HMF [HMF/Pd=25], 704.6 mg of 17.4 wt.% H_2SO_4 solution in H_2O (122.6 mg (1.25 mmol) H_2SO_4), addition of deaerated H_2O for 141.9 g of aqueous reaction mixture, [Pd]=150 ppm, T: 70°C, P_{CO}: 5 bar, t: 20 h.
[b] No metallic palladium formation.
[c] Determined by HPLC on the basis of HMF.

Table 6
The carbonylation and reduction of HMF with $Pd(tppts)_3$. Addition of different bases and protonic acids

Run [a]	Base or acid added (mmol)	Conversion (mol %)	Selectivity (mol %)	
			FFA	MF
6/1	H_2SO_4 (0.00)	37	74	26
6/2	H_2SO_4 (0.75)	80	74	25
6/3	H_2SO_4 (1.00)	85	73	27
6/4	H_2SO_4 (1.25)	90	72	28
6/5	H_2SO_4 (1.50)	79	70	29
6/6	p-$CH_3C_6H_4SO_3H$ (0.75)	78	75	24
6/7	HCl (0.75)	76	71	29
6/8	CF_3COOH (0.75)	75	76	23
6/9	$HClO_4$ (0.75)	69	75	25
6/10 [b]	HBr (0.75)	77	48	52
6/11	HI (0.75)	54	0	100
6/12	$CH_3CH_2NH_2$ (0.75)	0	0	0
6/13	CH_3COONa (0.75)	0	0	0

[a] Reaction conditions: 35.5 mg (0.2 mmol) $PdCl_2$, 681.8 mg (1.2 mmol) tppts [P/Pd=6], addition of base or acid; 0.63 g (5 mmol) HMF [HMF/Pd=25]; addition of deaerated H_2O for 141.9 g of reaction mixture, [Pd]=150 ppm; T: 70°C, P_{CO}; 5 bar, t: 20 h.
[b] Conversion (based on CO): 79%.

the tppts/Pd ratio and the presence of a Brønsted acid cocatalyst (Tables 5 and 6). No catalytic activity was observed in the absence of tppts and low catalytic activity resulted when the tppts ligand was added either in relatively small amounts or in large excess. The highest yield of FFA was obtained with a P/Pd ratio of 6. According to the literature [5] the carbonylation of substituted benzyl alcohols in organic solvents under acidic conditions using the hydrophobic catalyst Pd/PPh_3 leads to the formation of metallic palladium. Under our conditions we did not observe metallic palladium formation in the carbonylation of HMF at a tppts/Pd ratio larger than 6. The stability of the Pd/tppts catalyst suggests that the Pd–P bond in the Pd/tppts catalyst in aqueous medium is more stable than in the Pd/PPh_3 systems in organic solvents.

The addition of a Brønsted acid is necessary for facile carbonylation, without addition of acid a low conversion resulted (Table 6). The optimum acid/HMF molar ratio in the case of H_2SO_4 was found to be 1:4 (run 6/4). The nature of the acid had a marked effect on the selectivity. Acids of weakly or non coordinating anions, such as trifluoroacetic, p-toluenesulfonic and sulfuric acid, afforded mainly carbonylation. The selectivity decreases dramatically with acids of strongly coordinating anions such as hydrogen bromide and hydrogen iodide. With the latter the only product observed was the reduction product, MF, in essentially quantitative selectivity. No reaction was

observed when $Pd(tppts)_3$ was employed in combination with a base (e.g. $CH_3CH_2NH_2$ or CH_3COONa).

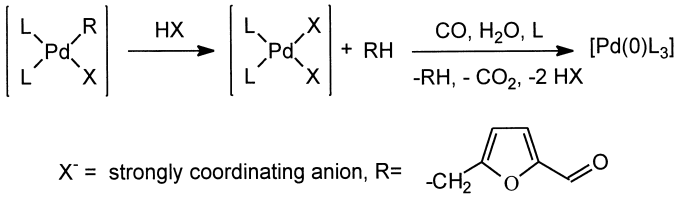
Blank runs showed that MF is not formed by reaction of HMF with acids e.g. HI in the absence of the $Pd(tppts)_3$ catalyst. The formation of MF under the carbonylation conditions amounts to a new type of catalytic reaction: the reduction of an alcohol with carbon monoxide and water to the corresponding hydrocarbon. This reduction is equivalent to hydrogenolysis of an alcohol group to a hydrocarbon without using hydrogen. The concomitant formation of a molecule of carbon dioxide was verified by gas chromatographic analysis. A possible alternative explanation – the water gas shift reaction followed by catalytic hydrogenation – can be excluded since no H_2 was detected in the gas phase and typical hydrogenation products of HMF were not observed.

The carbonylation of HMF is assumed to involve the same mechanism as that proposed for the carbonylation of benzyl alcohol (Scheme 3). We suggest that competing protonolysis of the palladium(II)-alkyl intermediate (Scheme 7) affords MF together with PdX_2L_2. The latter undergoes subsequent reduction by CO and addition of a tppts ligand to regenerate the $Pd(tppts)_3$-catalyst. Protonolysis is favored with strongly coordinating anions, e.g. iodide, which block coordination sites on the palladium and, hence, inhibit coordination of carbon monoxide. In contrast, protonolysis is strongly disfavored with weakly coordinating anions, i.e. when the palladium-alkyl species is cationic.

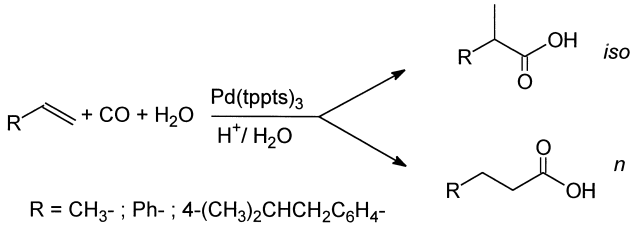
6. The hydrocarboxylation of α-olefins

Transition metal catalyzed hydrocarboxylation of olefins to carboxylic acids is a reaction of considerable industrial interest [11]. The reaction is applied, for example, in the synthesis of propanoic acid from ethene, using $Ni(CO)_4$ as a catalyst precursor under forcing reaction conditions (250–320°C, 100–300 bar). The palladium catalyzed hydrocarboxylation of olefins, in contrast, occurs under relatively mild conditions (70–120°C, 1–150 bar). Here again separation of the catalyst from the reaction mixture is cumbersome and constitutes a serious shortcoming of these processes.

As noted earlier, in the $Pd(tppts)_3$-catalyzed carbonylation of IBPE we observed the formation of small amounts of *p*-isobutylstyrene (IBS) which led us to surmise that the latter may be an intermediate in the reaction. We subsequently found that the hydrocarboxylation of IBS (Scheme 8), in the presence of $Pd(tppts)_3$ and *p*-toluenesulfonic acid as a cocatalyst, at 90°C and 50 bar, proceeds eight times faster than the carbonylation of IBPE. The catalyst activity was,



Scheme 7. The formation of MF when X is an strongly coordinating anion.



Scheme 8. The $Pd(tppts)_3$ catalyzed hydrocarboxylation of propene, styrene and IBS.

Table 7
The $Pd(tppts)_3$ catalyzed hydrocarboxylation of IBS, styrene and propene

Run [a]	Olefin	Olefin/Pd molar ratio	p-$CH_3C_6H_4SO_3H$ (mmol)	t (min)	T (°C)	Conversion (mol%)	Selectivity (mol%)		TOF (h^{-1})
							iso	n	
1 [b]	IBS	50	7	600	65	62	74	14 [c]	3
2 [b]	Styrene	50	7	600	65	100	56	33 [c]	5
3 [b]	Styrene	250	7	180	65	59	73	27	49
4 [b,e]	Propene	1000	0	30	110	12	43	57	239
5 [b,e]	Propene	1000	29	30	110	70	42	58	1390
6 [b,e]	Propene	1000	60	30	110	64	43	57	1284
7 [b,e]	Propene	1000	29	15	120	63	43	57	2507
8 [d,e]	Propene	1000	29	30	110	12	43	57	246

[a] Reaction conditions: 35.5 mg (0.2 mmol) of $PdCl_2$, tppts (tppts/Pd molar ratio=4; except runs 1 and 2 P/Pd=8), Brønsted acid, addition of deoxygenated distilled H_2O to give 141.9 g of aqueous reaction mixture, [Pd]=150 ppm, amount of olefin without addition of organic solvents; P=50 bar.
[b] No metallic palladium formation.
[c] Formation of heavy ends, presumably polymers of IBS or styrene.
[d] PPh_3 (0.8 mmol) instead of tppts, 116.0 g of 1.4-dioxane and 18.7 g of H_2O; black precipitate, probably metallic palladium.
[e] One phase after the reaction.

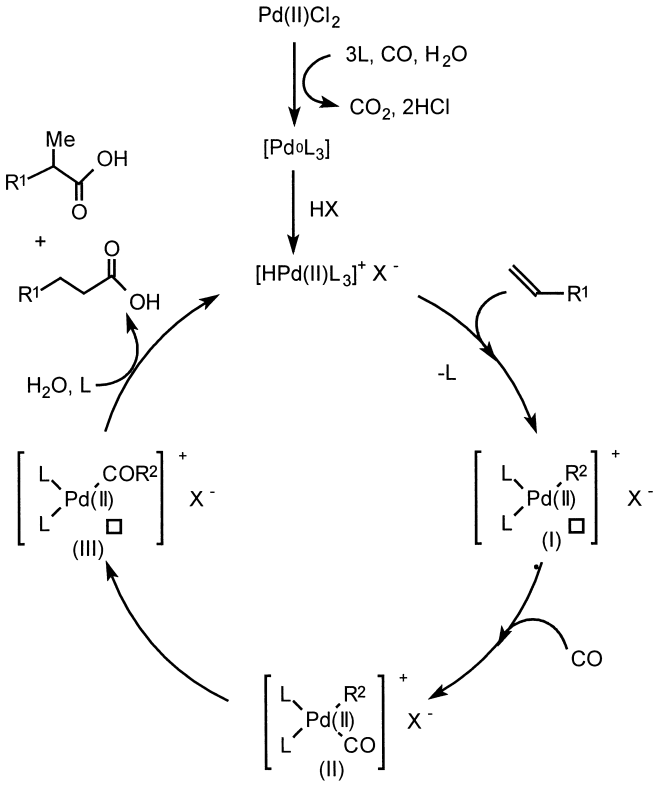
however, low (TOF=3 h^{-1}) probably due to the low solubility of IBS in water. This prompted us to investigate the hydrocarboxylation of the more water-soluble α-olefins, styrene and propene [12].

To prevent polymerization of the styrenes hydrocarboxylations were carried out at lower temperatures e.g. 65°C. In a typical experiment with IBS (Table 7), ibuprofen and its linear isomer were obtained at 62% IBS conversion with a selectivity of 74/14 (Ibuprofen/3-IPPA). In the hydrocarboxylation of styrene a much higher catalytic activity was observed; 58% conversion in 3 h (TOF=49 h^{-1}). We attribute the increase in catalytic activity to the better water-solubility of styrene in comparison with IBS.

Although propene is less reactive than styrene under the same conditions, it is less susceptible to polymerization which allows for more forcing conditions. At 110–120°C we observed unusually high activities in the hydrocarboxylation of propene (TOF>2500 h^{-1}). The n/iso ratio of the carboxylic acid products was ca. 60/40. As expected, no reaction was observed in the absence of tppts or in the presence of a base, such as sodium acetate or sodium hydroxide. Without addition of a Brønsted acid (note that 2 equivalents HCl are formed during the catalyst preparation) we observed a lower catalytic activity. The activity of $Pd(tppts)_3$ was also strongly influenced by the nature of the anion of the added Brønsted acid (c.f. the carbonylation of benzylic alcohols). Acids of weakly coordinating anions, e.g. p-$CH_3C_6H_4SO_3H$ or CF_3COOH, were effective while with acids of strongly coordinating anions, e.g. HI, no reaction took place.

In a comparison of Pd/tppts in water with Pd/PPh_3 in aqueous dioxane, [13] we found that Pd/tppts was significantly more active (TOF=1390 h^{-1} vs. 246 h^{-1}) and stable whereas in the Pd/PPh_3-catalyzed reaction the formation of a black precipitate indicated the decomposition of the catalyst.

For the hydrocarboxylation reactions catalyzed by $Pd(tppts)_3$ we propose the catalytic cycle depicted in Scheme 9. By analogy with related palladium chemistry, we assume that oxidative addition of HX to $Pd(tppts)_3$ forms the cationic palladium tppts hydride $[L_3Pd(II)H]^+$ which is the catalytically active species [14]. Dissociation of a tppts ligand is followed, successively, by olefin coordination, olefin insertion into the Pd–H bond to give intermediate I, CO coordination, migratory insertion and nucleophilic attack of H_2O on the acyl intermediate III to give carboxylic acid and, after coordination of a tppts ligand, the initial hydride intermediate. Markownikov addition of Pd–H species to the olefin leads to the branched carboxylic acid and anti Markownikov addition to the linear product (Scheme 5). When X is a strongly coordinating anion, such as I^-, the free coordination site in I is occupied, inhibiting coordination of CO.



Scheme 9. Proposed mechanism for the $Pd(tppts)_3$ catalyzed hydrocarboxylation of propene, styrene and IBS.

A possible explanation for the higher catalytic activity of Pd/tppts compared with Pd/PPh_3 in this reaction is that the lower basicity of tppts facilitates nucleophilic attack of H_2O on the acyl intermediate III. This hydrolysis reaction is considered to be the rate determining step, in analogy to the proposed nucleophilic attack of ROH on palladium-acyl intermediates in organic soluble carbonylations [15].

7. Concluding remarks

In summary we have developed an efficient method to prepare the water-soluble catalyst $Pd(tppts)_3$ and we have shown that it is an active catalyst in the carbonylation of benzylic type alcohols and in the hydrocarboxylation of α-olefins. The carbonylation of IBPE can be performed in a biphasic aqueous system which offers the possibility to remove the catalyst from the product mixture in a facile manner. Although ibuprofen selectivities are lower than in the (optimized) process using Pd/PPh_3 in organic media, further optimization of the biphasic system may bring selectivities up to the same level.

The conversion of the renewable HMF to a useful product is performed in a completely aqueous medium, the first example of such a carbonylation in water. In the presence of Brønsted acids, based on a strongly coordination anion, we observed a new type of reaction: the reduction of an alcohol to an alkane.

And finally, we showed in the hydrocarboxylation of propene that a water-soluble catalyst can have a very high activity, in this case much higher than in organic systems. Further exploration of this interesting field of catalysis will undoubtedly afford more

examples of efficient and environmentally friendly technologies.

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