# Catalytic Conversions in Water: a Novel Carbonylation Reaction Catalysed by Palladium Trisulfonated Triphenylphosphine Complexes

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The renewable basic chemical 5-hydroxymethylfurfural (HMF) is selectively carbonylated to the new compound 5-formylfuran-2-acetic acid using a water-soluble palladium complex of trisulfonated triphenylphosphine as the catalyst in an acidic aqueous medium at 70 °C and 5 bar CO pressure; when hydrogen iodide is the acid component, the reaction follows a different course and HMF is selectively reduced to 5-methylfurfural.

Trisulfonated triphenylphosphine (tppts) complexes of transition metals are highly soluble in water, which provides for their facile recovery from organic reaction products, by simple phase separation, in catalytic processes. The $RhH(CO)(tppts)_3$ complex, for example, is applied industrially in catalytic, two-phase hydroformylation of propene.[1] We have investigated the carbonylation of 5-hydroxymethylfurfural (HMF) in aqueous medium in the presence of a water-soluble palladium-tppts catalyst. HMF is readily obtained from various carbohydrate sources, such as fructose, and contains both alcohol and aldehyde functionalities in addition to a heteroaromatic ring.[2] To our knowledge, this is the first example of a catalytic carbonylation using transition metal tppts complexes in a completely aqueous medium. Owing to their low solubility in organic solvents the use of an aqueous medium is essential for carbohydrate conversions and also has environmental benefits.

Table 1 lists typical results obtained in the carbonylation of HMF in water at 70 °C and 5 bar CO pressure in the presence of tppts and various Brønsted acids. No catalytic activity was observed in the absence of tppts or acid. Chemoselective carbonylation of HMF was observed to afford the previously undescribed 5-formylfuran-2-acetic acid (FFA)† as the sole carbonylation product. Under these conditions the only byproduct observed was 5-methylfurfural (MF)‡ resulting from reduction of the HMF (see Scheme 1). Levulinic acid (4-oxopentanoic acid) and formic acid, the hydrolysis products of HMF, were observed only in strongly acidic media (pH −0.18) at higher temperatures (100 °C).

**Table 1** Carbonylation and reduction of HMF by Pd/tppts complexes at 150 ppm Pd in the aqueous solution[a]

| Run | P/Pd molar ratio | Acid Type | Acid (mmol) | Conversion[b] /mol% | Selectivity[b] /mol % FFA | MF |
|---|---|---|---|---|---|---|
| 1 | 0 | $H_2SO_4$ | (1.25) | 0 | 0 | 0 |
| 2 | 2 | $H_2SO_4$ | (1.25) | 1 | 22.4 | 77.3 |
| 3 | 4 | $H_2SO_4$ | (1.25) | 53 | 64.9 | 34.4 |
| 4 | 6 | $H_2SO_4$ | (1.25) | 90 | 71.6 | 27.9 |
| 5[c] | 8 | $H_2SO_4$ | (1.25) | 71 | 72.2 | 27.2 |
| 6[c] | 12 | $H_2SO_4$ | (1.25) | 40 | 72.9 | 26.3 |
| 7 | 6 | $H_2SO_4$ | (1.25) | 49 | 72.8 | 27.0 |
| 8[c] | 8 | $H_3PO_4$ | (0.4) | 24 | 83.2 | 16.2 |
| 9 | 6 | $H_3PO_4$ | (0.75) | 70 | 77.3 | 22.2 |
| 10 | 6 | $CF_3COOH$ | (0.75) | 75 | 76.0 | 23.4 |
| 11 | 6 | p-$CH_3C_6H_4SO_3H$ | (0.75) | 78 | 75.0 | 24.3 |
| 12 | 6 | $H_2SO_4$ | (0.75) | 80 | 74.3 | 25.1 |
| 13 | 6 | HCl | (0.75) | 76 | 70.8 | 28.6 |
| 14[d] | 6 | HBr | (0.75) | 77 | 47.8 | 51.5 |
| 15 | 6 | HI | (0.75) | 54 | 0 | 99.8 |

[a] All reactions were conducted in a Hastelloy C autoclave (300 ml) with catalyst solution [$PdCl_2$ (35.5 mg; 0.2 mmol) and tppts dissolved in 50 g of deaerated distilled $H_2O$ within 25 min complexation at room temp. pH = 2.1–2.9], amount of HMF (0.63 g; 5 mmol), protonic acid and addition of deaerated $H_2O$ for 141.9 g of reaction mixture, [Pd] = 150 ppm, HMF/Pd = 25; except run 7, HMF/Pd = 100 and run 8, HMF/Pd = 50; at 70 °C, $P_{CO}$ = 5 bar, $t$ 20 h; except run 8, $P_{CO}$ = 10 bar; after the reaction: pH = 1.4–1.9; black autoclave wall presumed to be metallic palladium. [b] Determined by HPLC on the basis of HMF. [c] No metallic palladium formation. [d] Conversion (based on CO) = 79%.

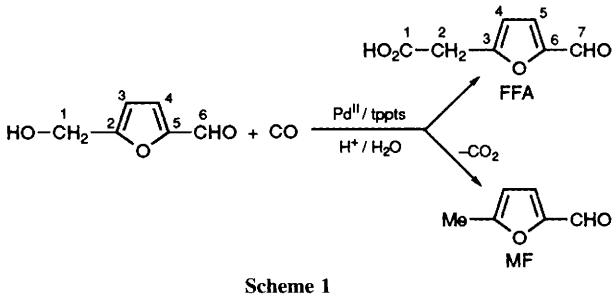
The mild conditions (70 °C; 5 bar) contrast with the more forcing conditions (110–150 °C; 50–140 bar) required for analogous carbonylations of benzylic alcohols catalysed by $Pd/Ph_3P$ complexes in organic solvents.[3] Both the activity and selectivity of HMF carbonylation were influenced by the tppts : Pd molar ratio, maximum efficiency being observed for tppts/Pd = 6 (run 4).

The nature of the anion of the acid component markedly influenced the selectivity. Acids of weakly or non coordinating anions, such as phosphoric, trifluoroacetic, *p*-toluenesulfonic, sulfuric and hexafluorophosphoric acid, afforded mainly carbonylation. A slightly lower selectivity was observed with hydrogen chloride but the selectivity decreased 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. A blank run demonstrated that no MF was formed from reaction of HMF with HI in the absence of the Pd/tppts catalyst. The formation of MF under these conditions amounts to a new type of catalytic reaction: reduction of an alcohol to the corresponding hydrocarbon according to the stoichiometry, eqn. (1).

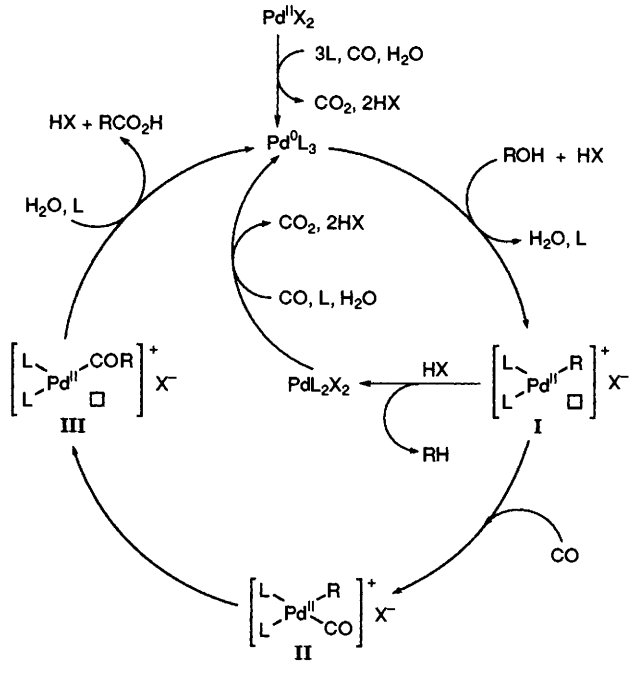
$$ROH + CO \rightarrow RH + CO_2 \quad (1)$$

The concomitant formation of a molecule of carbon dioxide was demonstrated by GC. A possible alternative explanation —the water-gas shift reaction followed by catalytic hydrogenation—can be excluded since no hydrogenation products of HMF were observed and no $H_2$ was detected in the gas phase. Indeed, the quantitative selectivity of the HMF reduction to MF is even more remarkable when one considers that HMF contains a reactive aldehyde group. Thus, catalytic hydrogenation of HMF[4] in the presence of metal catalysts in aqueous media affords products of hydrogenation of the aldehyde moiety and the diene system as well as hydrogenolysis of the furan ring.

To explain the observed results we propose the catalytic cycle depicted in Scheme 2. Although the catalyst is added as a palladium(II) salt (usually $PdCl_2$) the actual catalyst is a palladium(0) tppts complex, formed *in situ*. Thus, independent experiments (to be reported in detail elsewhere) showed that the tppts ligand and CO in $H_2O$ reduces palladium(II) to




Scheme 1




**Scheme 2** L = tppts, ROH = HMF

palladium(0) under the reaction conditions with formation of $Pd(tppts)_3$, which is a new and more efficient route for the synthesis of the $Pd(tppts)_3 \cdot 9H_2O$ complex.[5] This is followed, successively, by oxidative addition of RX to $PdL_3$, CO coordination, CO insertion into the Pd–C σ bond of intermediate **II**, and nucleophilic attack of $H_2O$ on the carbon atom of the acyl intermediate **III** to give FFA and at the same time regenerate the catalyst. When $X^-$ is a strongly coordinating anion, coordination of CO is less favourable and intermediate **I** undergoes protonolysis to give RH and $PdL_2X_2$. The latter undergoes subsequent reduction by CO to regenerate the palladium(0) catalyst. Replacement of tppts by the more basic disulfonated triphenylphosphine increases the electron density on the palladium centre of the species **I**, the conversion drops dramatically and MF is the major product. Using the much more basic monosulfonated triphenylphosphine ligand only traces of FFA and MF were obtained.

FFA is an interesting precursor for the manufacture of 2,5-furandiacetic acid and 5-carboxyfuran-2-acetic acid, which could form polymers *e.g.* polyesters and polyamides, the latter being comparable with the well-known terephthalic acid- and isophthalic acid-based polyesters.

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## Footnotes

† FFA has been isolated from the tppts-free reaction mixture by column chromatography using as adsorbent silica gel 60 and eluting with methanol/EtOAc = 1/2 and fully characterised based on $^{13}C$ and $^1H$ NMR, IR, MS, LC/MS and elemental analysis. Resonance multiplicities, chemical shifts, coupling constants and attached proton test for NMR spectra, and elemental analysis are consistent with the proposed structure.

*Selected data* for FFA: $^{13}C$ NMR (100.57 MHz; $D_2O$) δ 178.0 (C-1), 38.8 (C-2), 152.9 (C-3), 113.0 (C-4), 129.3 (C-5), 161.4 (C-6), 181.4 (C-7); The numbering system is that in Scheme 1. $^1H$ NMR (399.95 MHz; $D_2O$) 3.66 (s, 2H, 2-H), 6.48 (d, $^3J_{4\text{-H},5\text{-H}}$ 3.57 Hz, 1H, 4-H), 7.47 (d, 1H, 5-H), 9.32 (s, 1H, 7-H); IR (KBr pellet), $\nu_{max}/cm^{-1}$ 3430 (br, νO–H), 3120 (w, νC=C–H), 2980–2840 (m, $\nu_{as,s}$ $CH_2$), 1665 [vs, νC=O(aldehyde)], 1580 [br, vs, νC=O(acid)], 1518 (m, νC=C), 1422 (s, δO–H), 1282 [m, νC–O(acid)], 1028 [m, νC–O(furan)]; MS *m/z* = 44 (base peak, $CO_2$), 110 (FFA-$CO_2$), 208 (FFA.$3H_2O$); 60, 94 (McLafferty ions); LC/MS *m/z* = 155 [base peak, FFA (+1)], 173 [FFA.$H_2O$ (+1)].

*Selected data* for HMF: $^{13}C$ NMR (100.57 MHz; $D_2O$) 57.6 (C-1), 153.2 (C-2), 112.4 (C-3), 128.3 (C-4), 162.9 (C-5), 181.8 (C-6); $^1H$ NMR (399.95 MHz; $D_2O$) 4.62 (s, 2H, 1-H), 6.60 (d, $^3J_{3\text{-H},4\text{-H}}$ 3.59 Hz, 1H, 3-H), 7.44 (d, 1H, 4-H), 9.36 (s, 1H, 6-H); IR (KBr pellet) 3410 (br, νO–H), 3135 (w, νC=C–H), 2940–2860 (m, $\nu_{as,s}$ $CH_2$), 1676 (vs, νC=O), 1527 (m, νC=C), 1402 (m, δO–H), 1198 [m, νC–O(alcohol)], 1028 [m, νC–O(furan)].

‡ MF was identified by comparison of spectral data with data for authentic sample.

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