# Catalytic Conversions in Water: $^{17}O$, $\{^1H\}^{31}P$ and $^{35}Cl$ NMR Study of a Novel Stoichiometric Redox Reaction Between $PdCl_2$, tppts and $H_2O$ [tppts = $P(C_6H_4$-*m*-$SO_3Na)_3$]

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$^{17}O$, $\{^1H\}^{31}P$ and $^{35}Cl$ NMR are used to investigate the mechanism of the reaction of $PdCl_2$ with tppts [tppts = $P(C_6H_4$-*m*-$SO_3Na)_3$] in $^{17}O$ enriched water to give the novel complex $[PdCl(tppts)_3]^+$ **1**, which is reduced quantitatively to $Pd(tppts)_3$ **2** with tppts (8 d, 25 °C); with CO (2 bar) reduction to **2** is quantitative in 5 min at 25 °C.

The use of water soluble transition metal complexes, *e.g.* with tppts ligands, in two-phase systems is gaining importance since it combines the advantages of homogeneous and heterogeneous catalysis. This 'heterogenization' of homogeneous catalysts is employed industrially in the Ruhrchemie–Rhône-Poulenc process for the two-phase hydroformylation of propene using a water soluble $RhH(CO)(tppts)_3$ catalyst (300 000 tpa).[1] Moreover, catalytic conversions in aqueous media are environmentally attractive. Recently, we reported[2] that the $Pd(tppts)_3$ **2** complex catalyses the carbonylation of the renewable raw material 5-hydroxymethylfurfural (HMF) to 5-formylfuran-2-acetic acid under mild conditions in a completely aqueous medium.

We now report the use of $^{17}O$, $\{^1H\}^{31}P$ and $^{35}Cl$ NMR to study the *in situ* formation of palladium tppts complexes in aqueous solution. To our knowledge, this is the first application of $^{17}O$ NMR spectroscopy in studies of such water-soluble complexes. We also found a one-step synthesis of the novel cationic complex $[PdCl(tppts)_3]^+$ **1** from $PdCl_2$ and tppts in $H_2O$. In sharp contrast, the reported synthesis of the analogous hydrophobic $[PdCl(PPh_3)_3]^+$ **3** from $PdCl_2$ in organic solvents involves 4 steps *via* formation of $PdCl_2(PhCN)_2$, *trans*-$PdCl_2(PPh_3)_2$ and $[Pd(\mu\text{-}Cl)(PPh_3)_2]_2^{2+}$ intermediates.[3]

A mixture of $PdCl_2$ (0.15 mmol) and tppts (0.9 mmol) was dissolved in 40 g of deaerated distilled water, by stirring under an argon atmosphere for 25 min at room temp., to give a bright yellow solution. $\{^1H\}^{31}P$ NMR analysis [80.98 MHz; 25 °C; $D_2O$] showed that 47% of the tppts had been converted to **1** [δ + 33.98 (t, 1P, P-*trans*-Cl), 30.76 (d, 2P, P-*cis*-Cl), $^2J_{P,P}$ 14.6 Hz] which was identified by comparison with the reported[3,4] NMR spectrum of $[PdCl(PPh_3)_3]^+$ **3**, 46% was unreacted [δ − 5.33 (s)] and 7% had been converted to tppts-oxide (tpptso) [δ + 34.56 (s)]. The signal of free tppts was very broad ($\Delta\nu_{\frac{1}{2}}$ = 140 Hz) compared to the 6.8 Hz line width in the doublet of **1** and 1.8 Hz of tpptso. This is probably due to exchange between the counter anion of **1** which is presumably an anionic sulfonate group of tppts and free tppts or proton exchange involving the sulfonate groups of all species present in solution. The $^{35}Cl$ NMR [39.18 MHz; 25 °C; $D_2O$] revealed the presence of ionic chloride as a sharp signal at δ − 3.9. The FT far-IR spectrum (PE pellet) exhibited a band at 313 $cm^{-1}$(m) which could be attributed to ν(Pd–Cl) of **1** [ν(Pd–Cl) of **3** at 312 $cm^{-1}$].[3] Attempts to purify **1** by column chromatography (silica gel 60 deactivated by $H_2O$; mobile phase: $CH_3OH$–$H_2O$ = 6 : 1) were unsuccessful as it underwent dissociation of tppts to give *trans*-$PdCl_2(tppts)_2$[5] also in the presence of $NaBF_4$.

The reduction of **1** to **2** was followed by $\{^1H\}^{31}P$, $^{35}Cl$ and $^{17}O$ NMR spectroscopy. A solution of **1**, prepared from $PdCl_2$ (0.15 mmol) and tppts (0.9 mmol) in a deaerated mixture of $D_2O$ (2.25 ml) and $H_2O$ (0.75 ml) containing 20 atom% $^{17}O$ (CIL, Massachusetts, USA), was allowed to stand for 8 d at room temp. $\{^1H\}^{31}P$ NMR analysis (161.89 MHz; 25 °C) of the solution revealed that **1** had been quantitatively reduced to **2** [δ + 22.91 (s)][7]† with concomitant formation of tpptso at δ + 34.52(s). The peak integrals showed that 50% of the tppts (3 equiv.) had formed complex **2**, 27% remained unreacted and 23% (1.38 equiv.) had been oxidized to tpptso.‡

The $^{17}O$ NMR (54.22 MHz; 95 °C) of the mixture revealed the presence of $^{17}O$ labelled P=O group of tpptso at δ + 49.8 ± 0.5 (d, $^1J_{O,P}$ 100 ± 20 Hz) [Fig. 1(*a*)] which was assigned by comparison with data reported for $^{17}O{=}PPh_3$.[9*a*] A further $^{17}O$ signal at +174.9 ± 0.5(s) was assigned to the $-SO_3^-$ groups of **2**, tppts and tpptso by comparison with $^{17}O$ chemical shifts of $-SO_3$ groups in similar hydrophobic compounds, *e.g.* *p*-$MeC_6H_4SO_3Me$.[9*b*]

A blank $^{17}O$ NMR experiment demonstrated no incorporation of $^{17}O$ into tpptso in the reaction of $PdCl_2$ with tppts in $D_2O$–$H_2O$ (75 : 25) in the absence of added $H_2{}^{17}O$ [Fig. 1(*b*)]. The signal at δ 0.0 ± 0.5 is assigned to naturally abundant $^{17}O$ in $H_2O$ (natural abundance: 0.037%) and at δ +174.7 ± 0.5(s) to naturally abundant $^{17}O$ in the $-SO_3^-$ groups of **2**, tppts and tpptso.

These $^{17}O$ NMR experiments unambiguously demonstrate that water is the source of oxygen in the redox reaction depicted in Scheme 1. The pH of the reaction mixture after formation of **1** was 2.14 and after 8 d it decreased to 1.08, consistent with the

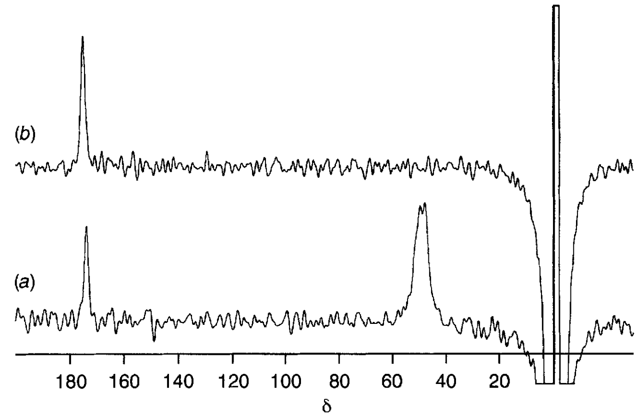
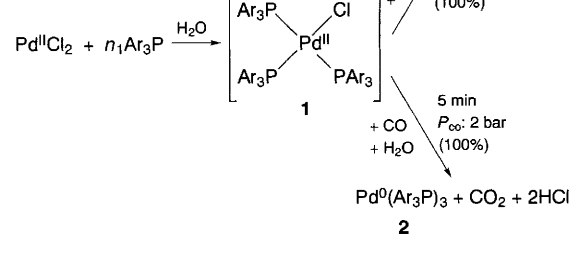


**Fig. 1** $^{17}O$ NMR spectrum of the redox reaction between $PdCl_2$, tppts and $H_2O$ after 8 d in: (*a*) $D_2O$–$H_2O$ (75 : 25) with 5 atom% $^{17}O$ enrichment (enhanced resolution by applying weighting of the fid with a shifted sine bell function; measurement after evaporation of the $^{17}O$ enriched and diluted in $^{17}O$ depleted $H_2O$; (*b*) $D_2O$–$H_2O$ (75 : 25)



**Scheme 1** Ar = $C_6H_4$-*m*-$SO_3^-$ $Na^+$

formation of HCl according to Scheme 1. The formation of $Cl^-$ was confirmed by $^{35}Cl$ NMR [39.20 MHz; 25 °C] $\delta$ + 0.2 (s).

A more attractive synthesis of **2** involves the facile reduction of **1** by CO in $H_2O$, with concomitant formation of $CO_2$ and HCl (Scheme 1). Reduction of **1** by $H_2$—formed *via* the water gas shift reaction—can be excluded since no $H_2$ was detected in the gas phase by GC. A solution of **1**, prepared from $PdCl_2$ (0.15 mmol) and tppts (0.9 mmol) dissolved in 40 g of deaerated distilled $H_2O$, with a pH of 3.52 was charged into a Hastelloy C autoclave under argon. After a number of pressurising–depressurising cycles with CO to remove air, the autoclave was pressured to 2 bar at 25 °C with stirring. The $\{^1H\}^{31}P$ NMR spectrum of a sample after 5 min of reaction revealed the formation of **2** (50%),† free tppts (41%) and tpptso (9%).‡ The pH of the reaction mixture after 5 min under CO was 2.24 indicating the formation of HCl. The formation of $CO_2$ was demonstrated by GC analysis. These results demonstrate the potential of $^{17}O$ NMR for the direct observation of reactions of transition metal complexes in aqueous solutions and open new possibilities for the identification of hydroxometal complexes such as $Rh(OH)(tppts)_3 \cdot 9H_2O$ which have been previously proposed on the basis of elemental analysis.[10]

The readily accessible $[PdCl(tppts)_3]^+$ complex is especially interesting since it is isoelectronic with the hydrophobic Wilkinson's catalyst, $RhCl(PPh_3)_3$, and may find wide applications in catalytic reactions in aqueous media as well as in two-phase systems.

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## Footnotes

† The singlet of **2** is slightly broadened, which cannot be explained by ligand exchange of **2** with free tppts but is probably due to formation of $Pd^0(tppts)_2Cl_2^{2-}$ intermediates [$Pd^0(PPh_3)_2Cl_2^{2-}$ at $\delta$ +23.15 (s)[7]]. The signal of **2** became a sharp singlet after dilution of the sample.

‡ The formation of higher amounts of tpptso can be explained by $PdCl_2$ catalysed oxidation of tppts with traces of oxygen in the water. Similar reactions occur with other transition metal salts.[5]

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