Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Speciation of $Pd(OAc)_2$ in Ligandless Suzuki-Miyaura Reactions

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Content

(i) Changes in UV absorption in the presence of water and boronic acid.

Using anhydrous solvent, a slow process was observed upon mixing solution of $Pd(OAc)_2$ and boronic acid. On the other hand, an immediate change in absorbance was observed when water was introduced (5% and 20%), even in the absence of boronic acid.

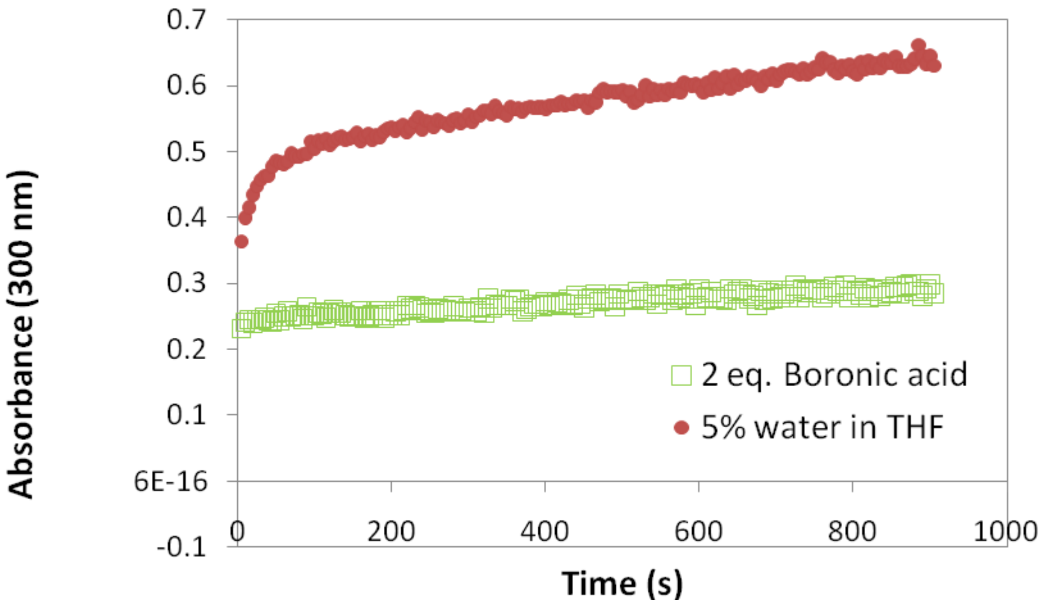


Figure S1. Absorbance vs time at 300 nm (data recorded over 900 s, sampling rate = 2 Hz)

(ii) Kinetic model

$$A \xrightarrow{k_{1obs}} B \xrightarrow{k_2} C$$

Scheme S1. Kinetic model (A = $Pd(OAc)_2$, B = activated Pd species, and C = Pd-nanoparticles)

To directly fit the observable (absorbance at λ = 300 nm), extinction coefficients were assigned for each species (A, B and C).

Table S1. Mixing volumes, in μL

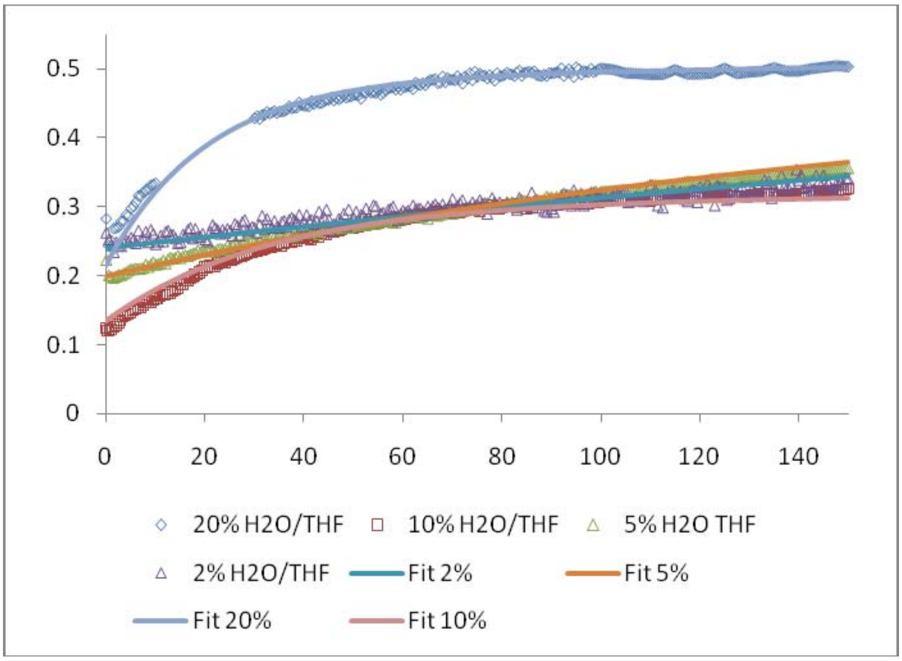
Exp.	% H_2O	$Pd(OAc)_2$ 8.91 mM	H_2O in THF (20%)	H_2O	$[Pd(OAc)_2]$ [mM]
1	2	90	10	0	8.02

2	5	75	25	0	6.68
3	10	50	50	0	4.45
4	20	100	0	25	7.13

(iii) Fitting of kinetic data

The kinetic model was fitted using Berkeley Maddona™ Modelling and Analysis of Dynamic System (Figure S2). A full set of kinetic measurements (Abs vs time, Table 1) were fitted using the same set of parameters ($k_{1\text{obs}}$, k_2, and extinction coefficients A1, A2 and A3 for A, B and C respectively) to simultaneously optimise these parameters for different runs using 5%, 10% 20% and 40% v/v water in THF. Four data sets of different runs in table 1 (approximately 220 data points each, trimmed to reduce the relative weight of the second step in fitting) were fitted simultaneously for 8 parameters (4 different $k_{1\text{obs}}$, k2, A1, A2 and A3). Pathlength information was included in A1, A2 and A3 and the total solution absorbance calculated as:

$$A = [A]*A1 + [B]*A2 + [C]*A3$$



$k_{1\text{obs}} = 2.58 \times 10^{-3}$
($2\%\ H_2O/THF$)

$k_{1\text{obs}} = 6.35 \times 10^{-3}$
($5\%\ H_2O/THF$)

$k_{1\text{obs}} = 30.56 \times 10^{-3}$
($10\%\ H_2O/THF$)

$k_{1\text{obs}} = 49.37 \times 10^{-3}$
($20\%\ H_2O/THF$)

$k_2 = 1.69 \times 10^{-3}$

A1 = 30.00

A2 = 68.67

A3 = 78.76

Figure S2. Data fitting.

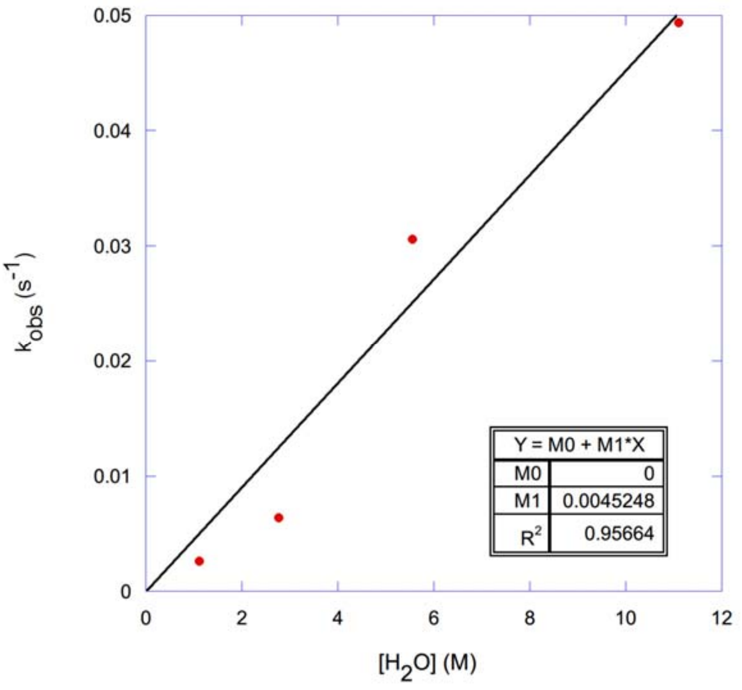


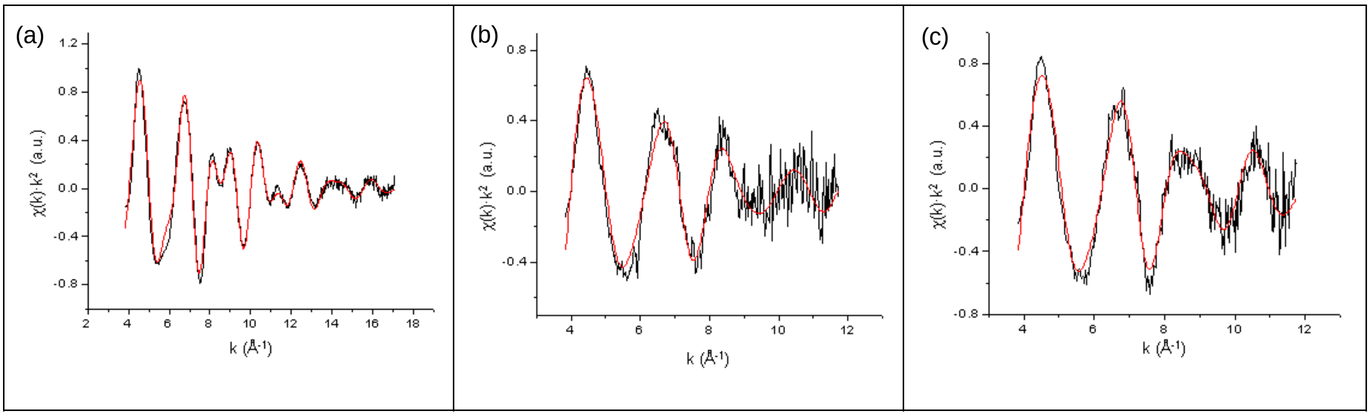
Figure S3. Plotting k_{1obs} *vs* $[H_2O]$.

$k_{1obs} = k_1{*}[H_2O]$, which leads to $k_1 = 4.52 \times 10^{-3}$ L.mole^{-1}.s^{-1}, comparable to k_2.

(iv) EXAFS analysis.

Figure 5 in the manuscript shows k^2-weighted Fourier-transformed (FT) amplitudes of the EXAFS signal of $Pd(OAc)_2$ in the solid state, 40 mM of $Pd(OAc)_2$ in toluene and 40 mM $Pd(OAc)_2$ in DMF. Table 2 in the main text gives the structural parameters that resulted from the EXAFS minimization procedure.[1] Herein, Figure S3 shows the best fits in k^2 space of the above-mention samples.

Figure S3. Pd k-edge EXAFS signals (black) and corresponding fits (red) in k^2-space of (a) $Pd(OAc)_2$ in the solid state; (b) 40 mM of $Pd(OAc)_2$ in toluene; and (c) 40 mM $Pd(OAc)_2$ in DMF.



The solid $Pd(OAc)_2$ structure fits well with the trimeric arrangement. The crystallographic data of the trimer presents Pd-O distances of 1.969-2.022 Å, Pd-C distances of 2.90-2.96 Å and Pd-Pd distances of 3.08-3.18 Å. The possibility of being a linear trimeric structure $[Pd_3(OAc)_4]$, as once was elucidated by powder diffraction,[2] was discarded because of the mismatch to the experimental data. In the case of the toluene and DMF solutions the situation is somehow different to the solid sample.

Principal Component Analysis (PCA) showed that the spectra contained 2 (or 3) independent components. It is difficult to discern between 2 or 3 components due to the low quality of experimental data at high k. Nonetheless, a third component was included in our analysis, as the estimated noise level of $\sigma=\pm0.005$ is already considerable.

Linear combinations of the two above-mentioned monomeric and trimeric Pd species together with a third component have been performed. The third component was considered as being either Pd particles or some sort of dimeric Pd acetate compound. Pd particles are commonly formed, in higher or lesser extent, as a consequence of the bright X-ray beam impinging on the sample and breaking the bonds around Pd atom. Also, dimeric structures are also plausible. Nevertheless, we could confirm that when either of these components were used in the analysis, the percentage of those were below 8%, which lies well below the limits of detection in an EXAFS experiment. Therefore, the addition of a third component did not influence the global outcome of the analysis. The linear combination results are shown in Table 3 in the manuscript.

References

[1] Stern, E. A. *Phys. Rev. B*, **1993**, *48*, 9825.

[2] Kirik, S. D.; Mulagaleev, R. F.; Blokhin, A. I. *Acta Cryst*. **2004**, *C60*, m449-m450.