

## Supplementary Information

### ***In situ* investigation of the oxidative addition in homogeneous Pd catalysts by synchronised time resolved UV-Vis/EXAFS.**

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#### **Figure 1**

The thick dotted line in Figure 1 was obtained by taking the difference between two XANES energy points (in this particular case, absorption at 24379 eV and absorption at 24365 eV) in the normalised time resolved spectra.

The times indicated for the two bands of the UV-Vis spectra (13 s for band at 491 nm and 25 s for the band at 432 nm) were obtained by fitting a first order exponential equation and multiplying the relaxation time ( $\tau$ ) by 3 (95% disappearance of signal). (Ref. <http://nmr.chem.indiana.edu/NMRguide/operation/t1t2.html>)

#### **Modelling in EXAFS analysis**

The small Debye-Waller factor ( $0.001 \text{ \AA}^2$ ) obtained for the Pd-C in model  $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$  (1) is probably due to an under-estimation of the coordination number of C on the Pd center. Here, a coordination of 2 C was considered for the model. However, at high temperatures, the mobility of the carbon chain of the dba ligand may have some contribution, having some conformation where additional carbon atoms remain closer than expected to the Pd center. Such low Debye-Waller factors have been also observed in similar systems (Ref. 4).

The 87% conversion of  $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$  into  $[(\text{PPh}_3)_2\text{PdPhI}]$  at  $t = 13 \text{ s}$ , was obtained by comparing the integrals of the Pd-I EXAFS peak ( $r \text{ (\AA)} = 2.1 - 2.9$ ) at  $t = 0 \text{ s}$ ,  $t = 13$  and  $t = 25 \text{ s}$ .

The models used for the EXAFS analysis of the starting compound  $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$  were derived from the following (the first one being the good model):

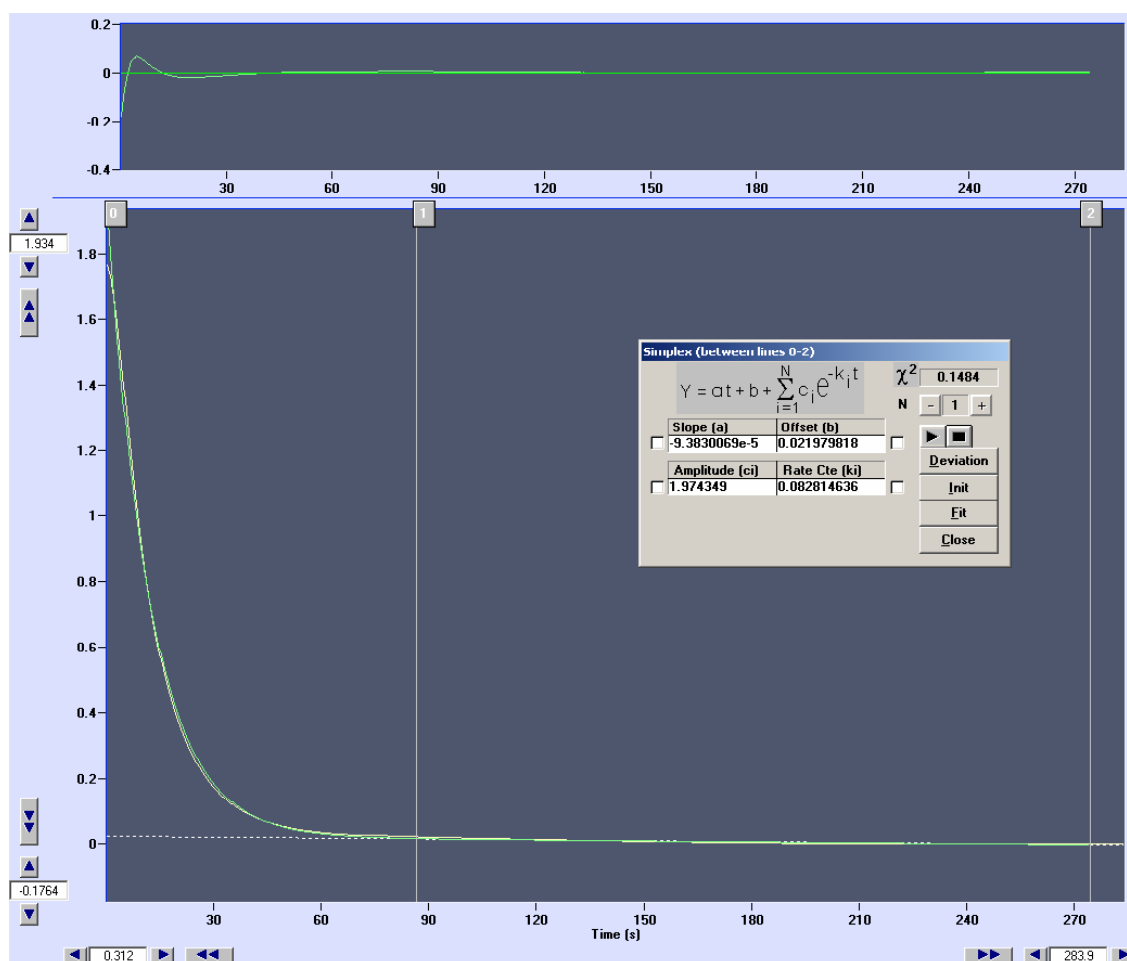
- $(\eta^2\text{-Dibenzylideneacetone})\text{-bis}(\text{tribenzylphosphine})\text{-palladium}$  methanol solvate (R. E. Marsh, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2004, **60**, 252)
- $(\mu_3\text{-Carbonyl})\text{-tris}((\mu_2\text{-bis}(\text{diphenylphosphino})\text{methane})\text{-palladium})\text{-bis}(\text{hexafluorophosphate})$  acetone solvate (R. Provencher, K. T. Aye, M. Drouin, J. Gagnon, N. Boudreault, P. D. Harvey, *Inorg. Chem.*, 1994, **33**, 3689)
- $\text{bis}(\mu_3\text{-}\eta^2, \eta^2\text{-Triphenylphosphine-P})\text{-bis}(\text{triphenylphosphine})\text{-tri-palladium}$  bis(tetrafluoroborate) isopropanol dichloromethane solvate (S. Kannan, A. J. James, P. R. Sharp, *J. Am. Chem. Soc.*, 1998, **120**, 215)

The models used for the EXAFS analysis of the final product [(PPh<sub>3</sub>)<sub>2</sub>PdPhI] were the following (the first one being the good model):

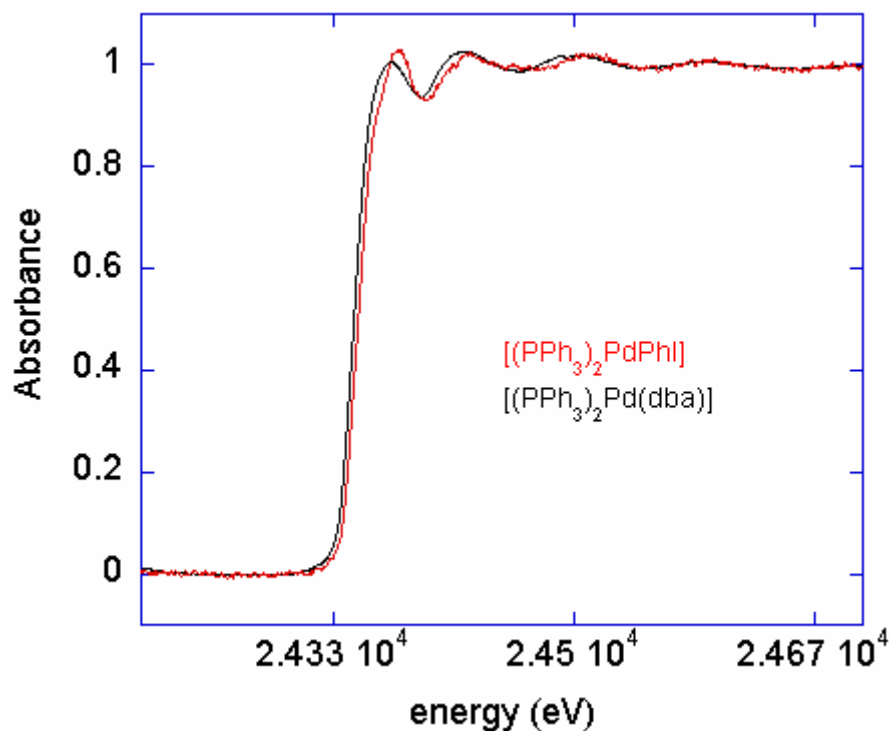
- Iodo-phenyl-bis(triphenylphosphine)-palladium(II) (J. P. Flemming, M. C. Pilon, O. Ya. Borbulevitch, M. Yu. Antipin, V. V. Grushin, *Inorg. Chim. Acta*, 1998, **280**, 87)
- Di-iodo-bis(triphenylphosphine) palladium(II) dichloromethane solvate (T. Debaerdemaeker, A. Kutoglu, G. Schmid, L. Weber, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1973, **29**, 1283)
- bis((μ<sub>2</sub>-Iodo)-benzoyl-triphenylphosphine-palladium) benzene solvate (V. V. Grushin, H. Alper, *Organometallics*, 1993, **12**, 1890)
- bis((μ<sub>2</sub>-Chloro)-bis(triphenylphosphine)-palladium(II)) bis(tetrafluoroborate) acetone solvate dehydrate (S. Ganguly, E. M. Georgiev, J. T. Mague, D. M. Roundhill, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 1169)
- bis(μ<sub>3</sub>-Chloro)-trichloro-tris(triphenylphosphine)-tri-palladium acetone solvate (K. Sugimoto, T. Kuroda-Sowa, S.-G. Yan, M. Maekawa, M. Munakata, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 414)

### Kinetic Data

The apparent global rates constants were obtained using the kinetic software BioKine version 4.27 from Bio-Logic SA, considering rate =  $k_{app}[(PPh_3)_2Pd(db)]$ , where  $k_{app} = k [PhI]_{excess}$ . The fitting of the UV-Vis curve at 491nm with a simplex algorithm is shown below:

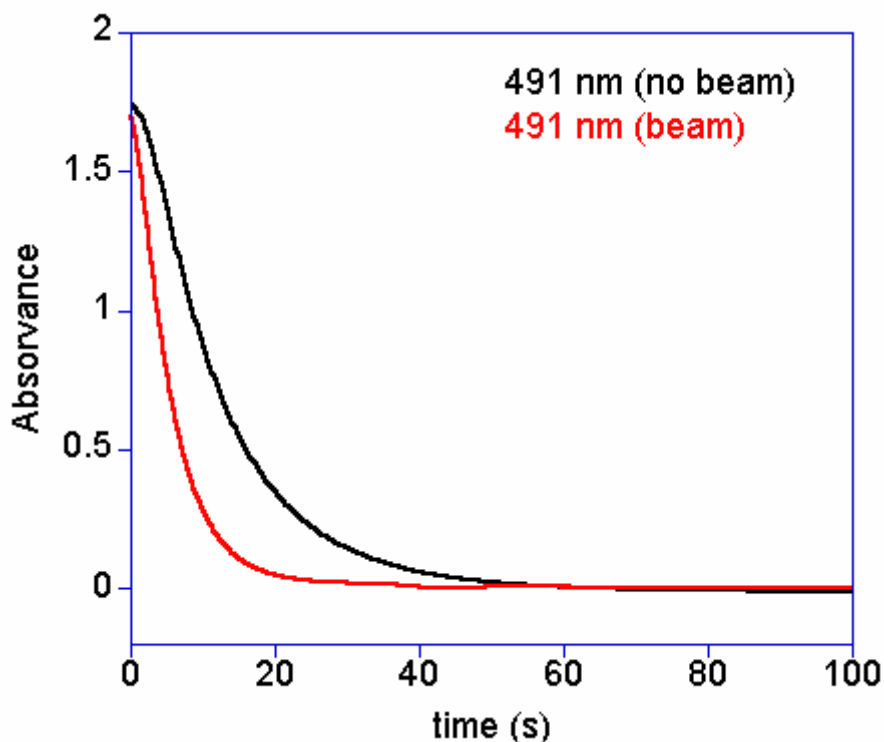


Supplementary Figure 1 shows the normalised EXAFS spectra of the starting and end product of the oxidative addition reaction  $[(\text{PPh}_3)_2\text{Pd}(\text{dba})] + 10 \text{ PhI}$  conducted at  $40^\circ\text{C}$  on ID24 (ESRF).



The blue spectrum represents the starting compound  $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$  (19 spectra of 200 ms each). The red spectrum represents the final product of the reaction, this being *trans*- $[(\text{PPh}_3)_2\text{PdPhI}]$  (29 spectra of 100 ms each).

Supplementary Figure 2 shows the accelerating effect of the X-ray beam on the oxidative addition (observable at 491 nm in the UV-Vis spectrum). There is no beam damage, nor decomposition of the compound, nor alteration of the reaction mechanism.

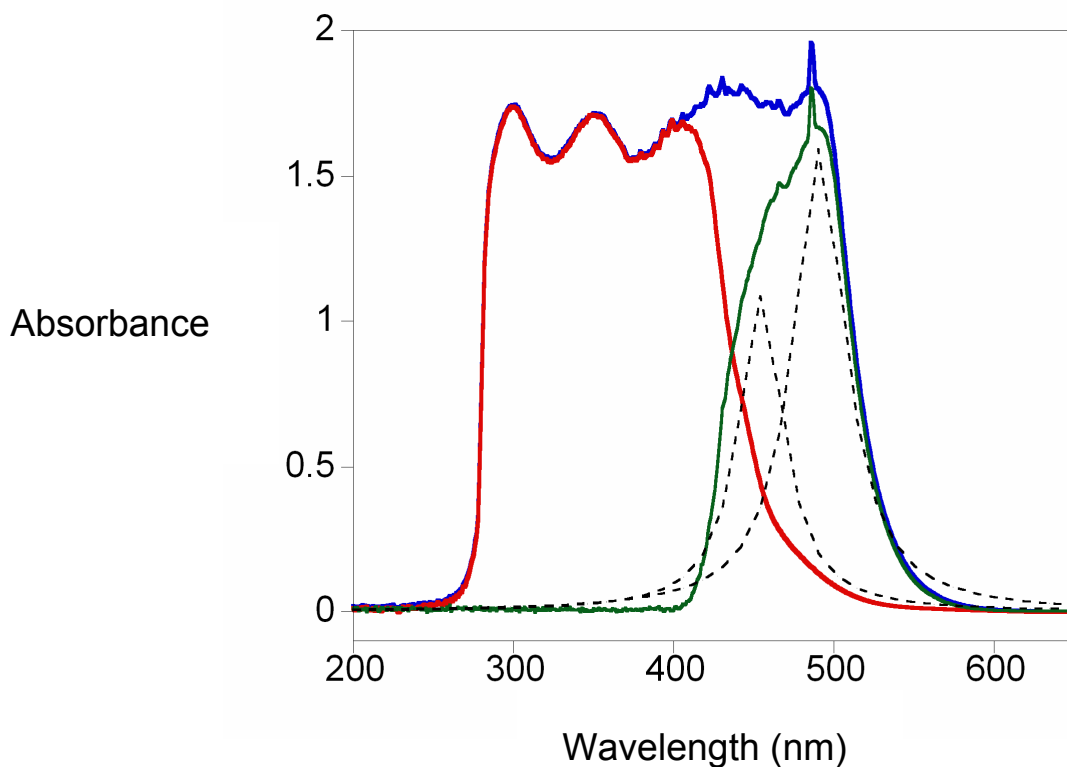


The doubling of the observed rate constant corresponds to a mild local heating effect due to the X-rays. Compared with the damage observed for a Cu system (ref. 8b), the stability of the Pd sample towards X-ray may arise from the intrinsic characteristics of the Pd system, from the use of toluene as solvent (it does not undergo radiolysis), from the absence of chlorine ligands (they may be involved in radical parasitic reactions), or from the lower flux received on the sample due to the specific experimental conditions.

However, other phosphine-based Pd catalysts did show clear and significant X-ray induced damage on the time scales required for experimentation. These included combinations of [Pd(dba)<sub>2</sub>] and [Pd(OAc)<sub>2</sub>] with different equivalents of 2-biphenyl-di(*tert*-butyl)phosphine, 1,3-Bis(2,6-di-*i*-propylphenyl)imidazolium chloride and tricyclohexylphosphine.

Therefore, extreme care needs to be exercised in making measurements of this type if reliable and quantitative structure function relationships are to be derived. The use, *in situ*, of a secondary, corroborating technique in these cases, should be thought of as mandatory rather than optional.

Supplementary Figure 3 shows the UV-Vis spectra of the starting compound and final product of the reaction.



The blue spectrum represents the starting material,  $[(PPh_3)_2Pd(dba)]$ . The red spectrum represents the final product of the reaction, *trans*- $[(PPh_3)_2PdPhI]$ . The green line is the difference between both blue and red spectra, and the dotted lines arise from the Lorentzian deconvolution of the difference spectrum.