



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Mechanistic and Kinetic Investigation of Palladium Catalysis by Stopped-flow/ED-XAFS Experiments

Experiment number:
CH1942**Beamline:****Date of experiment:**

from: 16/03/2005 to: 21/03/2005

Date of report:**Shifts:****Local contact(s):** Gemma Guilera*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

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Dr Meritxell Guinó

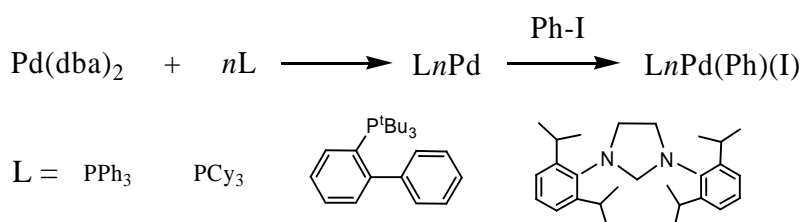
Dr Gemma Guilera* European Synchrotron Radiation Facility (ESRF, ID24), Grenoble, France

Dr Mark Newton

Report:

Energy dispersive EXAFS (EDE) was used to investigate the mechanism of the oxidative addition process of 10 equivalents of PhI (phenyl iodide) on several Pd catalysts (see Scheme1) in toluene with the stopped-flow/UV-Vis/EDE facility of ID24, which in turn was synchronised at the millisecond regime.

To the best of our knowledge, the oxidative addition reaction of Pd(0) complexes has never been investigated dynamically under *operando* conditions. Only in two instances has a similar set-up been applied: the study of copper catalysis, and an electron transfer reaction between iridium and cobalt.¹



Scheme 1. Oxidative addition reaction under study
(dba=dibenzylideneacetone, Ph=phenyl, Cy=cyclohexyl)

For this experiment the stopped-flow was adapted with Isolast o-rings in order to work with toluene as solvent.

First of all, the different Pd-based compounds and reactions were checked with the UV-Vis spectrometer (with and without x-ray beam) to account for possible decomposition of the sample or induced parasitic reactions by effect of the beam. From all the ligands examined only those compounds containing PPh₃ and PCy₃ did not suffer decomposition. As such, we decided to perform the experiments using triphenylphosphine (PPh₃) as a ligand. The final concentration of the (PPh₃)₂Pd(dba) solution was 40mM.

This concentration of the Pd precursor was verified off-line to follow the same reaction mechanism as for the lower catalytic concentrations.

The reaction was followed by EDE on the Pd K-edge (24.350 KeV) during 78s, at 40°C and with a time-resolution of 500ms/spectrum. A Si(311) polychromator was used. UV-Vis spectroscopy was synchronised with EDE.

The combination of these two complementary techniques allowed us to obtain structuro-kinetic correlations and to directly elucidate, for the first time, the reaction mechanism as being composed by two steps: the concomitant oxidative addition of PhI onto the $[(PPh_3)_2Pd(dba)]$ in a *cis* configuration, followed by *cis*-/*trans*- isomerisation. The oxidative addition process is distinguished indirectly by the UV-Vis as the loss of the dba ligand, and directly by the EXAFS analysis by the concomitant addition of phenyl iodide on the Pd center, as well as by the shift in the XANES region indicating a change of the degree of the palladium's oxidation state. The isomerisation is only detectable on the UV-Vis spectrum as the loss of a band due to the phosphine ligand reorganisation and agrees, qualitatively, with the formation of a compound with higher symmetry, i.e. from a C_s (*cis*-isomer) to a C_{2h} (*trans*-isomer) (see Figure1).

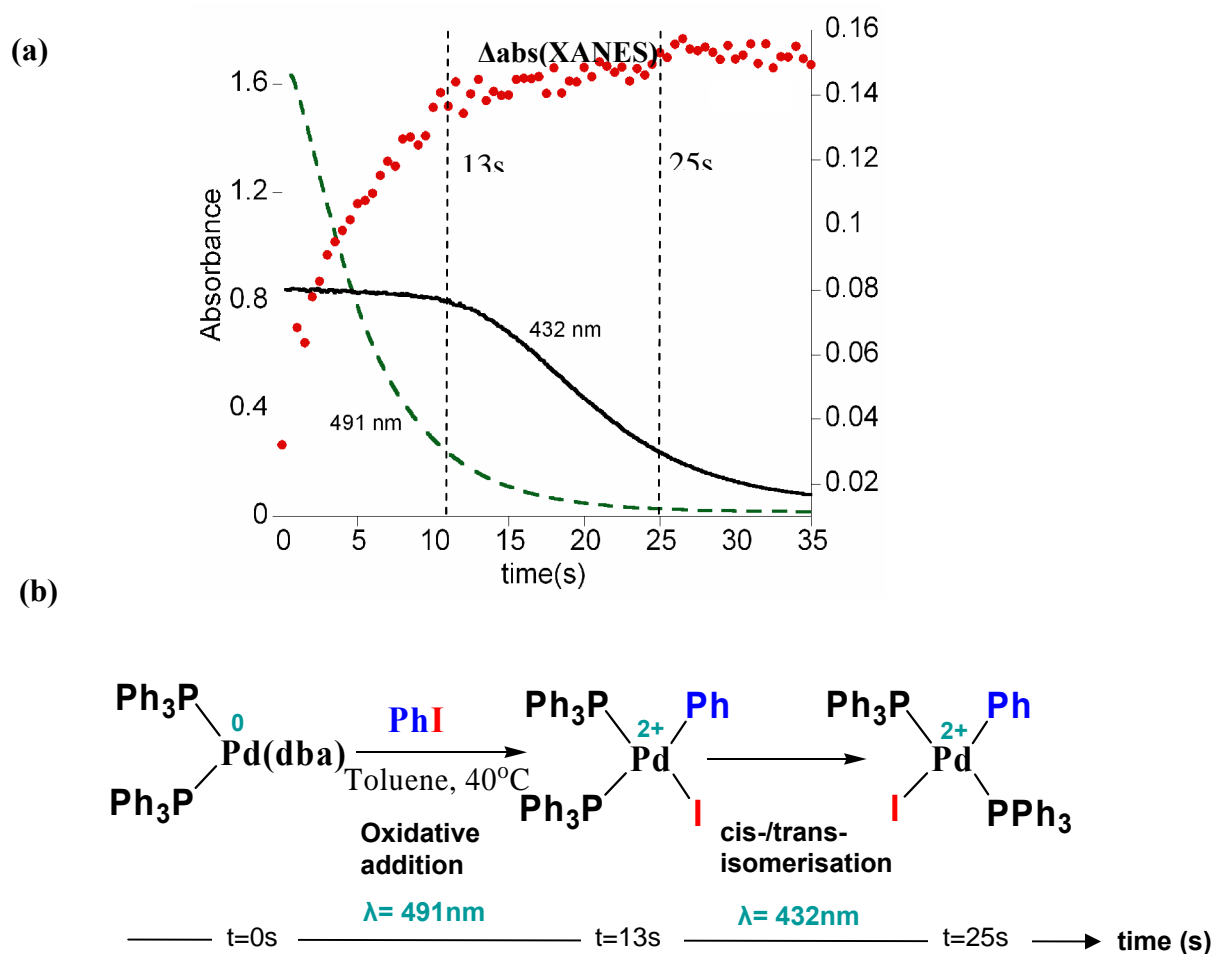


Fig. 1 (a) Real time variation of UV-Vis spectral bands (432 and 491 nm) and the corresponding XANES feature as 10 equivalents of PhI are added to the toluene solution of $[(PPh_3)_2Pd(dba)]$ (40 mM) at 40°C. (b) Schematic representation of the reaction mechanism.

Furthermore, it was observed that this reaction takes place gradually and there is no evidence for a significant existence of intermediate Pd species containing only one phosphine ligand, or bimolecular compounds, or any type of palladium cluster, as postulated in some instances²; yet the formation of these compounds cannot be completely ruled out, because of the averaging nature of the EXAFS technique.

References

- (a) S. Diaz-Moreno, D. T. Bowron, J. Evans, *Dalton Trans.*, 2005, **23**, 3814. (b) J. G. Mesu, A. M. J. van der Eerden, F. M. F. de Groot, B. M. Weckhuysen, *J. Phys. Chem. B*, 2005, **109**, 4042.

2. (a) C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.*, 1993, 115, 9531. (b) M. Tromp, J. R. A. Sietsma, J. A. van Bokhoven, G. P. F. van Strijdonck, R. J. van Haaren, A. M. van der Eerden, P. W. N. M. Leeuwen, D. C. Koningsberger, *Chem. Commun.*, 2003, 128.