

## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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.



	<b>Experiment title:</b> <b>Observation of transient intermediates in homogeneous Pd catalysis</b>	<b>Experiment number:</b> <b>CH 3543</b>
<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: 23 May 2012 to: 29 May 2012	<b>Date of report:</b> 01/09/2012
<b>Shifts:</b> 18	<b>Local contact(s):</b> Sakura Pascarelli	<i>Received at ESRF:</i>

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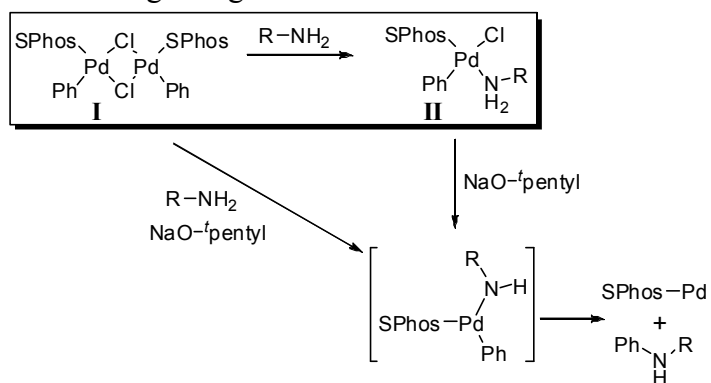
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**Report:**

**Aims**

The dimer **I** has been previously isolated and is known to react with primary amines to give the monomeric species **II**. The addition of both amine and an alkoxide base ultimately results in reductive elimination to give an aryl amine.

Previous studies at BM23 (CH-3315) and B18 at Diamond had given good static measurements of dimer **I** and the structures formed on addition of hexylamine, sodium *tert*-pentyloxyde or both. Using the fast time resolution capabilities of ID24 in conjunction with the stopped-flow/UV-vis apparatus available on the beamline we hoped to determine the presence of any intermediates formed during these chemical reactions. It was hoped that analysis of the data compared with the static standards previously obtained would allow some structural information about the intermediates to be extracted.

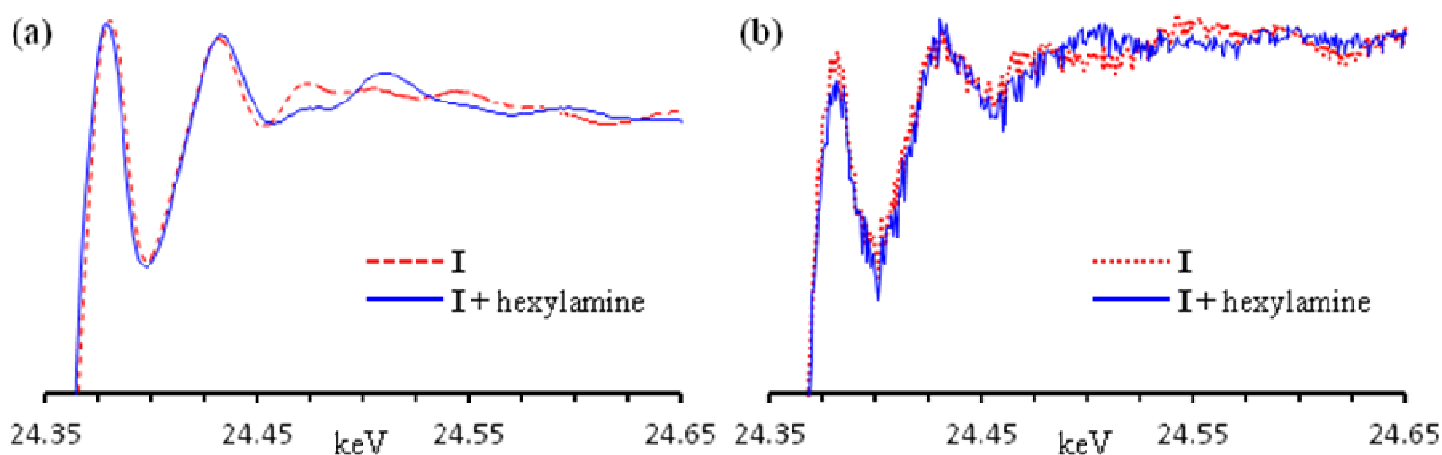


**Outcomes**

1. As first users on the new ID24 beamline, the allocated beamtime also represented the first commissioning of the beamline to use the stopped-flow/UV-vis with electronic triggering to allow high accuracy synchronisation of the chemical experiment with simultaneous recording of both UV-vis and XAS data. This process required optimisation of ESRF control software and electronic triggering as well as beam adjustments but was very successful resulting in an optimised system suitable for use by all users of this equipment at the beamline.

- The stopped-flow apparatus is fitted with Viton O-ring seals, which are primarily suited only to aqueous solutions. This severely limits the range of organic solvents which can be used with the apparatus. The experimental studies could therefore only be made in toluene. This had the side effect of preventing studies using sodium *tert*-pentyloxide due to its low solubility in this solvent.
- Studies on the addition of hexylamine to dimer **I** in toluene were conducted after optimisation of the timing and data collection parameters. The conversion of starting dimer **I** to monomer **II** could be easily identified in the recorded spectra. Unfortunately a very high degree of non-statistical noise was present severely limiting the interpretation of the data. The poor quality of the data limits any interpretation to the XANES region.

*Spectra of dimer I in toluene (a) and after the addition of hexylamine (b)*

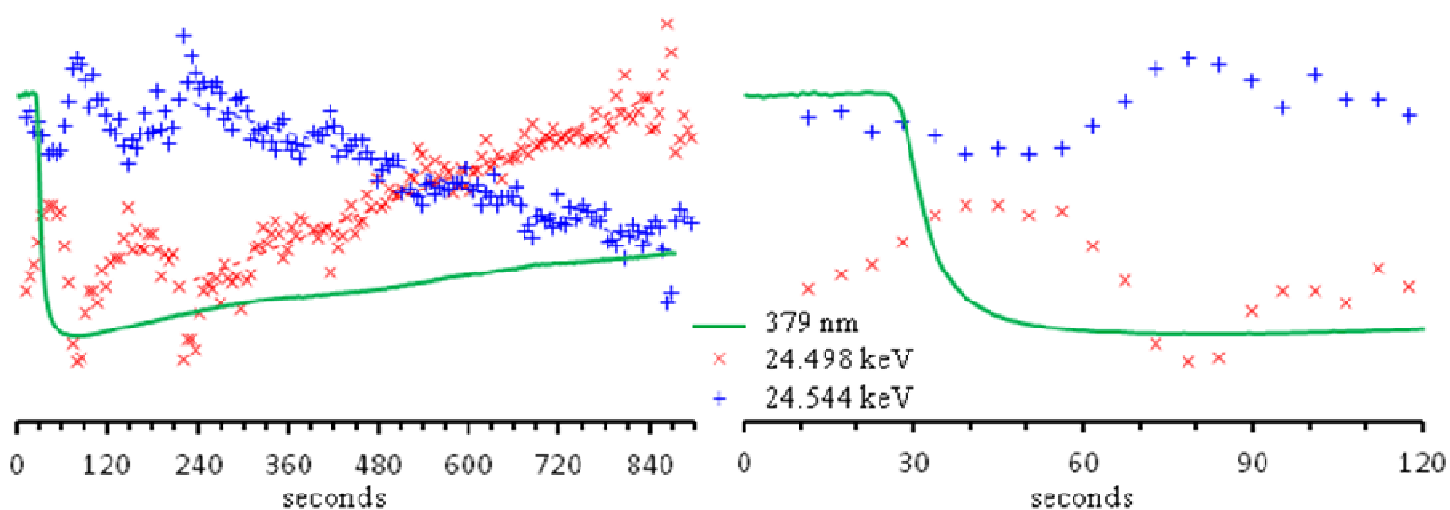


*Static spectra on scanning beamline B18*

*Time resolved spectra on dispersive beamline ID24*

The noise prevents an easy analysis of the reaction of the system over time although temporal analysis of key peaks in the spectra allows a broad trend to be observed. Crucially, we did not observe any decomposition of the sample in the beam, further confirming the suitability of this approach for studying these systems.

*Temporal evolution of two peaks in dispersive XAS and a peak in UV spectrum*



The likely source of the non-statistical noise is the use of a Bragg polychromator and the possibility of the asymmetric beam spot clipping the edges of the stopped-flow cuvette. At the high energies required for the Pd K-edge a Laue polychromator would be a better choice, but this has not yet been implemented on ID24. It is expected that with this improvement the noise that prevented a full analysis of the data could be largely

removed to allow full interpretation of the reaction under study. In addition, the improvement in the quality of the data would allow analysis of a wider range of the data including the EXAFS region.

In addition, the replacement of the stopped-flow O-rings with a material more suitable for the study of homogeneous catalysis in organic solvents would allow other solvents to be used which would allow the studies with sodium *tert*-pentyloxyde to be performed. This modification would also widen the scope of this equipment on the beamline.

### **Summary**

- Stopped-flow/UV-vis apparatus commissioned with electronic triggering by beamline software. Experimental setup of this system proved suitable for use with new ID24.
- The data obtained demonstrated the suitability of the new ID24 beamline for studying homogeneous catalytic systems at the Pd K-edge. The system chosen does not decompose in the beam.
- The conversion of dimer **I** to monomer **II** was observed. Unfortunately the data was of insufficient quality to allow a detailed analysis of the sample composition to be made with a high degree of confidence (eg. using linear combinations or principle component analysis).
- The advancement of this project relies on obtaining better quality data using the Laue polychromator which is expected to be commissioned on ID24 in early 2013.