



## 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.

**Experiment title:**

Elucidating transient intermediates in Pd-catalysed C-H activation reactions

**Experiment number:**

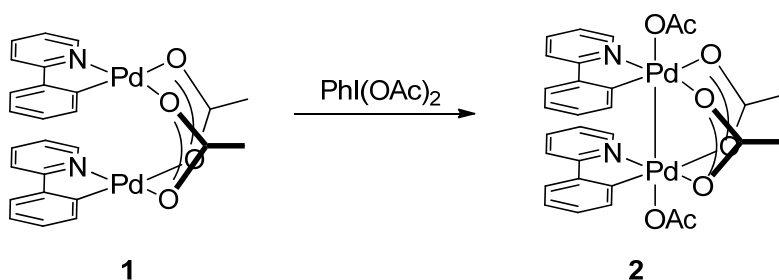
CH-3315

**Beamline:****Date of experiment:**

from: 13 July 2011 to: 19 July 2011

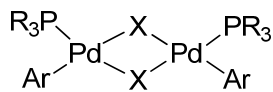
**Date of report:****Shifts:****Local contact(s):** Dr. Santiago FIGUEROA, Dr. Mark NEWTON.*Received at ESRF:***Names and affiliations of applicants** (\* indicates experimentalists):Dr. King Kuok (Mimi) Hii,<sup>a,\*</sup> Dr. Luis Adrio,<sup>a,\*</sup> Dr. John Brazier,<sup>a,\*</sup> Dr. Bao Nguyen,<sup>a,\*</sup>  
Dr. Santiago Figueroa<sup>a</sup>Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, U.K.<sup>b</sup>ESRF, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France.**Report:**

The Pd(II) dimer **1**, formed from the palladation of Pd(OAc)<sub>2</sub> with 2-phenylpyridine, can undergo oxidation to form Pd(III) dimer **2** (Scheme 1). An earlier attempt to examine this at the SuperSAXS beamline (X10DA) at the Swiss Light Source in the scanning mode (July 2010) met with only partial success. While an oxidation process is evident, the low flux of the beamline at the Pd K-edge did not allow the acquisition of sufficient quality data to confirm the solution structure of the oxidation product. By using the higher flux on beamline BM23, we hoped to be able to acquire structures of the Pd species in catalytically more relevant concentrations (1-20 mM) and, if possible, to conduct time-resolved studies.

**Scheme 1.** Oxidation of cyclometallated Pd(II) to a Pd(III) dimer.

We also made contingency for a second reaction system to be examined in case of unforeseen problems with the original proposed experiment. This involved the examination of the

reaction between the monophosphine-ligated Pd dimer **3** (figure 1) with different amines and an alkoxide base in solvents of very different polarity. This has particular relevance to catalytic aryl amination reactions, an important class of C-X bond forming reaction which has been widely used academically and industrially for the synthesis of organic molecules.<sup>1</sup>



**3**, X = Cl, (a), Br (b)

**Figure 1.** Dimeric monophosphine palladium(II) complexes.

### Reaction examined:

1. The scanning EXAFS spectrum of a solution of complex **1** in dichloroethane (40 mM) were initially recorded in the stopped-flow cuvette. Due to a combination of the chlorinated solvent (extensive absorption) and the small size of the window (1 × 1 mm), the available flux was too low to enable good quality spectra to be acquired. By adopting a larger (10 × 10 mm) cuvette, and by switching to chlorobenzene as a solvent (to reduce absorbance of the X-ray beam), the signal-to-noise ratio can be increased to allow good-quality spectra to be acquired. However, this effectively ruled out the primary goal of the proposal, which was to conduct time-resolved studies at lower concentrations. Furthermore, the concentrated solution of complex **2** generated in chlorobenzene was not stable in the beam, requiring freshly prepared solutions for each round of acquisition. Faced with these difficulties, it was decided that we focus the bulk of our efforts on the contingency project, while leaving this part of the work for a later proposal, *e.g.* to harness the higher flux available via the smaller spot size of the upgraded ID24. In the meantime, the scanning spectra acquired were sufficient for us to complete the preliminary studies on the solution structures of oxidised Pd(III) species, and this will be submitted for publication within the next few months.

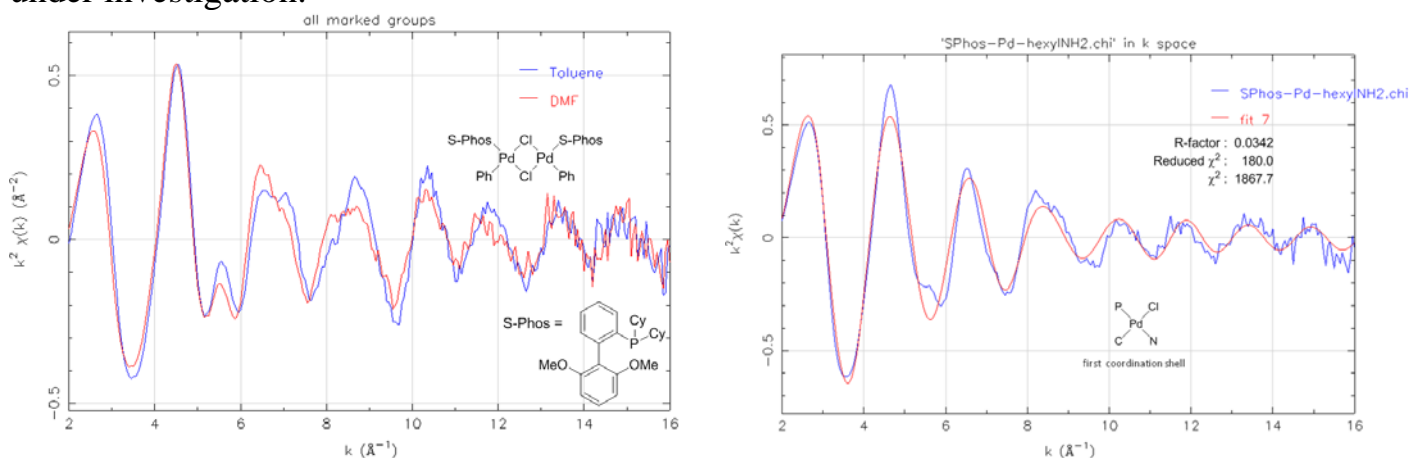
Due to the small sample window afforded by the stopped-flow equipment, we also decided to conduct the rest of our experiments in the scanning mode, acquiring solution spectra in larger quartz cells to maximise beam size.

2. Switching over to the chemistry of the dimeric complex **3**, further results were obtained. First, the spectrum of a solid sample of the chloro dimer complex **3** was recorded (for which the full structure has been previously elucidated by single crystal crystallography). The solution structure of the complex was subsequently examined in two solvents of different polarity: toluene and DMF (figure 2, left hand spectrum), as our earlier work has shown that this can have an important effect on the nuclearity of the complex.<sup>2</sup> Indeed, differences in the spectra were observed, suggesting that the complex does indeed adopt a different distribution of solution structures, which is expected to affect their subsequent catalytic activity. This provides a keenly sort after explanation for the commonly observed effects of solvent upon this class of reactions.

3. Addition of hexylamine to both of the above solutions led to the formation of the same product species. Preliminary fitting suggests cleavage of the chloro bridge by the amine, to

form a mono-nuclear, amine-coordinated complex (figure 2, right hand spectrum). This will be analysed in greater detail.

4. Addition of an alkoxide base also led to distinct changes in the coordination sphere of Pd, although in this case there is a more significant solvent dependence. This data is currently under investigation.



**Figure 2.** EXAS spectra of a mono-ligated palladium(II) complex, and its dissociation by an amine.

In summary, very useful data has been acquired using BM23 in the scanning mode. Time-resolved studies were not possible on this beamline due to the incompatibility of the stopped-flow equipment with the beam size. We propose that the acquisition of time-resolved spectra be conducted on the upgraded ID24, to try to delineate the kinetics of the process, and the possible involvement of a transient 3- or 5-coordinated intermediate due to the operation of a dissociative or associative process, respectively. This will form the basis of a future proposal. Preliminary results obtained with the scanning spectra will be disseminated via a publication within the next few months, with attendant studies conducted offline at Imperial College with complementary spectroscopic techniques such as NMR and UV-vis. Correlations with catalytic activity will also be made.

<sup>1</sup> (a) Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz, U. *Adv. Synth. Catal.* **2006**, *348*, 23. (b) Surry D. S.

Buchwald S. L. *Angew Chem. Int. Ed.* **2008**, *47*, 6338.

<sup>2</sup> L. A. Adrio, B. N. Nguyen, G. Guilera, A. G. Livingston and K. K. Hii, *Cat. Sci. Tech.*, **2011**, *in press*,

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