

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: Development and application of Energy Dispersive XAFS for Homogeneous Systems	Experiment number: CH-1275
Beamline: ID24	Date of experiment: 18-19/3/2002, 2-9/7/2002, 4-10/10/2002	Date of report: 11-12-2002
Shifts: 3/18/18	Local contact(s): Dr. Sakura Pascarelli, Dr. Steven Fiddy	<i>Received at ESRF:</i>
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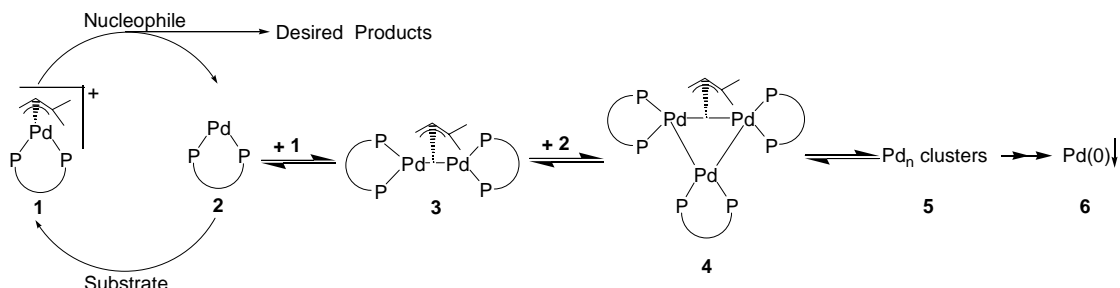
Report:

In close collaboration with the staff of ID24 (meeting in **March 2002**) we have build our own Energy Dispersive set-up, including Stopped Flow Apparatus, comparable to the one present at ID24 (to avoid problems with electronics etc...). In close contact with the manufacturing company, the Stopped Flow Apparatus was specially adapted; different parts were constructed from special materials, so all parts of the apparatus are now resistant to all (organic) solvents and reactants used.

During the first beamtime period (**July 2002**), the new set-up has been constructed on the beamline and tested. Hardly any problems with the new equipment and alignment were experienced. Unfortunately, the beam itself was very unstable for longer periods. However, experiments were performed resulting in data of good quality (both XANES and EXAFS).

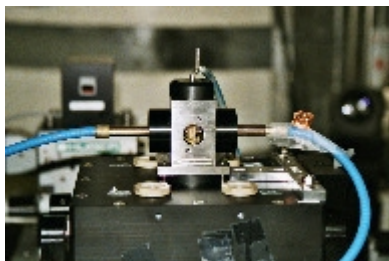
During this beamtime, the research of project CH-1065 and CH-1172 was continued. Energy Dispersive EXAFS (ED-EXAFS) at the Pd K-edge was used to study the deactivation behaviour of bidentate diphosphine ligand palladium catalysts, (P-P ligand)Pd, in the allylic amination reaction. The activity and selectivity of these Pd catalysts in the allylic substitution reaction was found to be influenced by the P-Pd-P angle, i.e. bite angle of the bidentate phosphine ligands. The results of the previous projects allowed us to perform more optimised experiments (better concentration ratios and time scales). Moreover, new experiments with additional nucleophiles and (P-P)-ligands were performed.

Since the Energy Dispersive set-up is portable, identical experiments (using the stopped flow apparatus) are performed at our own laboratory in Utrecht, now followed with optical fibre UV-Vis. Based on both time-resolved techniques, a mechanism for the deactivation reactions of the homogeneous (P-P ligand)Pd catalysts is proposed. These results are published in *Chemical Communications* [1].



Based on our EXAFS analysis and on literature of correlated Pd(P-P ligand) dimers and Pd(I) dimers, the dimer and trimer structures, as given in the Scheme above are proposed. During the allylic amination, the (P-P ligand)Pd(allyl) complex reacts to a (P-P ligand)Pd⁰-complex forming dimers, trimers and bigger clusters, eventually precipitating as palladium black. The rate of formation of dimers, trimers and further deactivation is observed to be a function of both ligand and solvent. For complexes with a small bite angle, both dimers and trimers are observed whereas for large bite angle ligands only dimers are formed. Increasing the polarity of the solvent decreases the deactivation rate. Both time-resolved techniques indicate the formation of dimers, trimers and possibly larger clusters directly from the start of the catalytic allylic amination reaction, thereby directly lowering the efficiency of the catalyst. The rate of formation of Pd clusters is lower compared with the stoichiometric reaction. The rates of formation and detailed structures of the different complexes are topic of investigation.

The combination of both Energy Dispersive XAFS and time-resolved UV-Vis was thus proven to be very successful in gaining insights in this homogeneous catalytic system. For the Pd-catalysed reactions as described above, both techniques were applied using the same set-up, however, not at the same time. Therefore, for the second beamtime (**October 2002**) the set-up was adjusted and new cuvettes were manufactured to be able to perform simultaneous measurements.



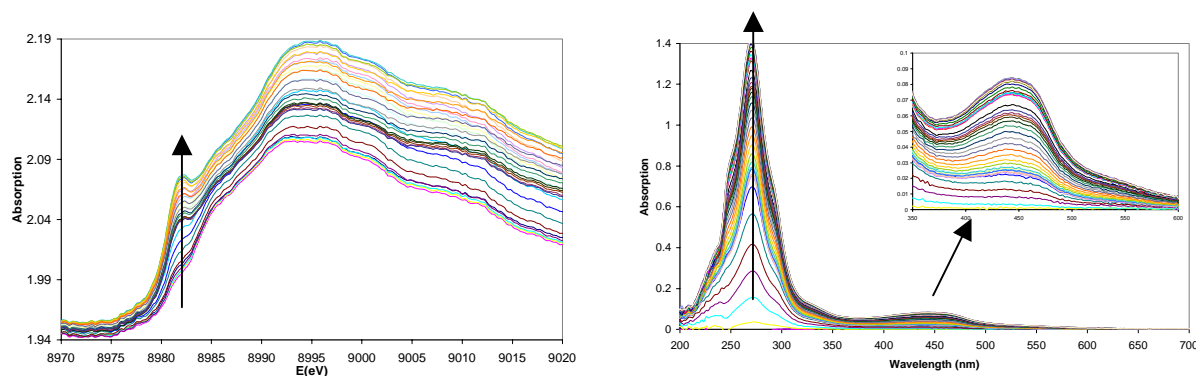
UV-Vis measurements using optical fibres (blue), perpendicular to ED-XAFS measurements

Using the new cuvette, with the X-rays and UV-Vis light perpendicular to each other, simultaneous ED-XAFS and UV-Vis experiments on the same sample are possible. A considerable amount of time was required to align the complete set-up, to optimise all triggering to start reaction and measurements simultaneously, and to optimise the beamline to obtain good to signal noise ratios.

A new system was now investigated. The formation of aryl-aryl bonds and aryl-hetero-atom bonds are among the most important tools of organic synthesis. Palladium complexes are by far the most used and studied catalysts for these reactions. Copper, however, is the most ancient transition metal used for the synthesis of biaryls. In many cases, palladium catalysts are more active and milder compared to copper. Some reactions, however, only proceed when a copper catalyst is used. Because of the lower costs of copper compared to palladium, the use of copper is when possible preferred over the use of palladium [2].

Simultaneous ED-XAFS measurements at the Cu K-edge and time-resolved UV-Vis measurements were performed to study Cu(I) and Cu(II) catalysed arylation reactions. The reactions were carried out in H₂O, NMP and acetonitrile at room temperature, with concentrations of ~10-20 mM Cu. XANES spectra of good quality were obtained with ~10 accumulations and detector exposure times of 60-200 ms. The reactions were monitored for ~1-5 minutes. Different Cu(I) and Cu(II) catalysts with and without phenantroline, and with PhB(OH)₂ and imidazole as substrates, are measured.

The analysis of all data is still in progress, but clear changes in both the UV-Vis spectra as the ED-XANES spectra (Figure below) are observed, giving us insights in changing oxidation states and geometry of the Cu catalysts and thereby in the occurring reaction mechanisms.



ED-XANES and time-resolved UV-Vis spectra

References

- [1]. M. Tromp, J. R. A. Sietsma, J. A. van Bokhoven, G. P. F. van Strijdonck, R. J. van Haaren, A. M. J. van der Eerden, P. W. N. M. van Leeuwen, D. C. Koningsberger, *Chem. Comm.* published on the web 5th of December **2002**.
- [2]. J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, 102, 1359.