

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: Study of the Catalytic Behaviour of Pd Catalysts with Bidentate Phosphine Ligands during the Allylic Alkylation Reaction using Energy Dispersive XAFS	Experiment number: CH-1172
Beamline: ID24	Date of experiment: from: 21 nov 01 to: 27 nov 01	Date of report: 30 Aug 2002
Shifts: 18	Local contact(s): Dr. Sofia Diaz Moreno	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Drs. Moniek Tromp* Dept. Inorganic Chemistry and Catalysis, Utrecht University, NL Dr. J.A. Van Bokhoven* Prof. Dr. Ir. D.C. Koningsberger A.M.J. van der Eerden* Dr. G.P.F. Van Strijdonck* Institute of Molecular Chemistry, University of Amsterdam, NL Prof. Dr. P.W.N.M. Van Leeuwen		

Report:

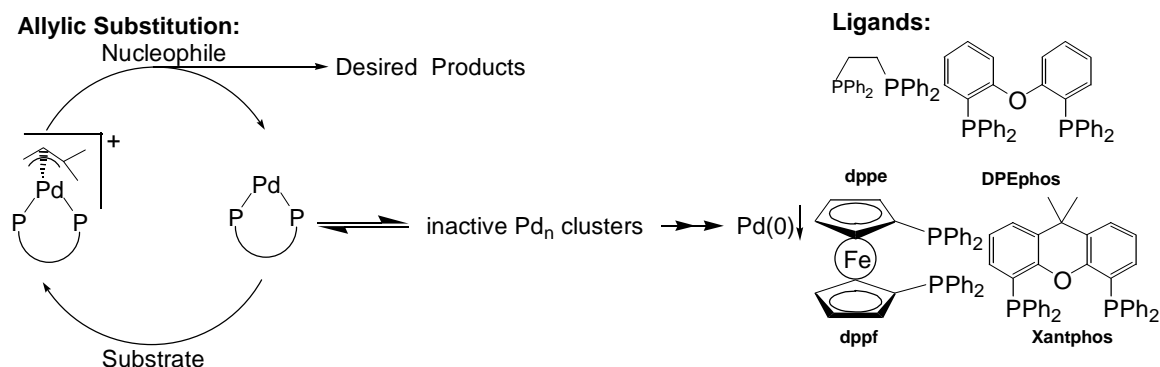
Energy Dispersive EXAFS (ED-EXAFS) at the Pd K-edge was used to study the deactivation behaviour of bidentate diphosphine ligand palladium catalysts, (P-P ligand)Pd, in the allylic amination reaction. The project was a follow-up of project CH-1065.

While for many applications initially the desired selectivities and reaction rates for these catalysts can be achieved, the stability of many palladium catalysts is too low for large-scale industrial processes. It is generally assumed that the deactivation of the catalyst occurs via clustering of intermediates in the catalytic cycle, eventually resulting in the precipitation of inactive palladium black. The stability towards the formation of inactive clusters and the performance of the catalysts are widely influenced by modification with a bidentate diphosphine ligand.

The palladium catalysed allylic substitution reaction is given in the scheme. We have prepared and isolated the catalytic (allyl)Pd(ligand) intermediate **1**, which we have already characterised in detail with NMR, X-ray crystallography [1] and 'normal' EXAFS in both solid state and solution [2].

To perform these homogeneous reactions, the stopped-flow XAS equipment present at ID24 was used. Both the stoichiometric (i.e. without substrate) and the catalytic allylic alkylation reaction were performed using the stopped flow cell. The reaction was carried out in different solvents, i.e. acetonitrile, acetone and THF at room temperature, with concentrations in the range of ~70 mM Pd. Piperidine was used as a nucleophile, allyl acetate

as the substrate. Spectra of reasonable quality were obtained with 10 accumulations and detector exposure times of 10 ms. The reactions were monitored for ~1-5 minutes, depending on the reactants.



Like for the previous project, a large part of the beamtime was necessary to properly focus the beam, align all equipment and resolve problems with the stopped flow cell since not all parts (O-rings and syringes) were resistant to all organic solvents.

Project CH-1065 already showed that the reaction rates of the allylic amination reaction and deactivation were dependent on the different ligands used. We now observed also a clear solvent dependency for the deactivation behaviour. While performing the reaction catalytically, similar XANES and EXAFS profiles were obtained, however, the rates decrease significantly.

The EXAFS analysis is very complicated since different Pd complexes are present in the reaction mixture. Initially, it is observed that the Pd(P-P-ligand) complex remains intact, while some Pd interactions come up. In time, it is clear that large Pd clusters are formed and the (P-P)ligand is decomposing, finally resulting in palladium precipitate in our cuvette [3]. The observed colour changes during the reaction and deactivation are also followed with time-resolved UV-Vis which shows initially clearly the formation of palladium dimers and trimers, while in time colloidal clusters and eventually palladium precipitate was observed [3]. The information obtained from UV-Vis is now used to further and in more detail analyse the ED-EXAFS spectra obtained.

References

- [1] R. J. van Haaren, K. Goubitz, H. Oevering, B. B. Coussens, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Inorg. Chem.*, **2001**, 40, 3363-3371.
- [2] M. Tromp, J. A. van Bokhoven, R. J. van Haaren, G. P. F. van Strijdonck, A. M. J. van der Eerden, P. W. N. M. van Leeuwen, D. C. Koningsberger, *J. Am. Chem. Soc.* **2002**, accepted.
- [3] 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, in prep.