EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

ESRF	**Experiment title:** Study of the Catalytic Behavior of Pd Catalysts with Bidentate Phosphine Ligands during the Allylic Alkylation Reaction using Energy Dispersive XAFS	**Experiment number**: CH-1065
Beamline: ID-24	**Date of experiment**: from: 20/06/01, 15:00hr to: 25/06/01, 23:00hr	**Date of report**: 19/02/2002 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. Sofia Diaz Moreno	

Names and affiliations of applicants (* indicates experimentalists):

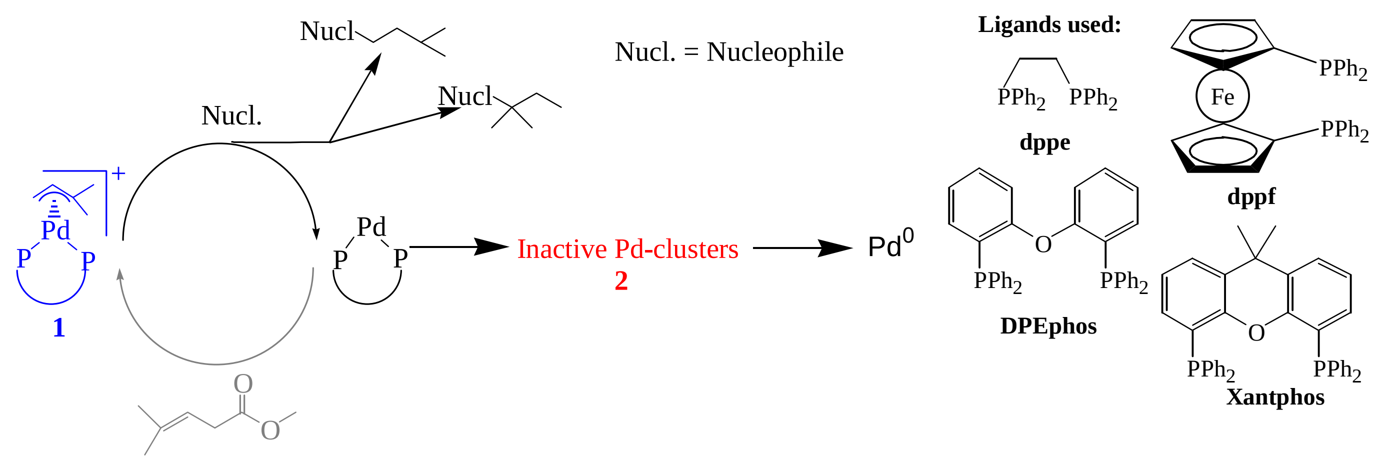
Drs. Moniek Tromp* Dept. Inorganic Chemistry and Catalysis, Utrecht University, NL
Dr. J.A. Van Bokhoven*
Prof. Dr. Ir. D.C. Koningsberger
A.M.J. van der Eerden*
Dr. G.P.F. Van Strijdonck* Institute of Molecular Chemistry, University of Amsterdam, NL
Prof. Dr. P.W.N.M. Van Leeuwen
Drs. R.J. Van Haaren

Report:

Energy Dispersive EXAFS (ED-EXAFS) at the Pd K-edge was used to study the deactivation behavior of bidentate diphosphine ligand palladium catalysts, (P-P ligand)Pd, in the allylic alkylation reaction. To perform these homogeneous reactions, the stopped-flow XAS equipment present at ID24 was used.

Palladium is the most widely used metal in transition metal catalyzed organic synthesis, as it is capable of catalyzing a wide variety of reactions [1]. While for many applications initially the desired selectivities and reaction rates 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 bidentate diphosphine ligand. Although a thorough understanding of the deactivation via clustering of homogeneous palladium catalysts is crucial for applications in large-scale industrial processes, so far, very few studies to this behavior have been reported. NMR techniques are not suitable to study the aggregation behavior of the catalyst, because the palladium atom itself can not be observed. The indirect study of clusters via the phosphorus atoms of the ligand (^{31}P-NMR) is hampered by the highly fluxional behavior of the clusters.

Allylic Alkylation, Catalytic Cycle



The palladium catalyzed allylic alkylation reaction [2] is given in the scheme above. We have prepared and isolated the catalytic (allyl)Pd(ligand) intermediate **1**, which we have already characterized in detail with NMR, X-ray crystallography [3] and ‘normal’ EXAFS in both solid state and solution.

The stochiometric (i.e. without substrate) allylic alkylation reaction is performed using the stopped flow cell. The reaction was carried out in acetone at room temperature, with concentrations in the range of 30-60 mM Pd, using piperidine as a nucleophile. Spectra of reasonable quality were obtained with 100 accumulations and detector exposure times of 10 ms. The reactions were monitored for ~10-20 minutes.

A large part of the beamtime was necessary to align all equipment and resolve problems with the stopped flow cell. The O-rings in the cell were not resistant to the organic solvent used which caused blockage of tubings and the cuvette and finally breakage of the cuvette. Therefore, part of the experiments had to be performed with a smaller cuvette with shorter pathlength, which resulted in very noisy (less quality) spectra.

The ED-EXAFS spectra showed that the reaction rate of the allylic alkylation and deactivation was dependent on the different ligands, see scheme, used. The data analysis/interpretation is still in progress since it is very complicated to separate the different palladium species present in the reaction mixture. However, differences in the shape of the edge (XANES region) and EXAFS are observed. Pd-Pd contributions are coming up, while during the first ~10 minutes no catalyst breakdown takes place. The observed color changes during reactions are not yet related to the different deactivated clusters formed, but it is hoped that further analysis of these Energy Dispersive data will give more insights.

References

[1] L. Hegedus, Transition Metals in the Synthesis of Organic Molecules, *University Science Books*, **1994**

[2] a) B. C. Hamann, J. F. Hartwig, *J. Am. Chem. Soc.*, **1998**, 3694-3703; b) R. J. van Haaren, H. Oevering, B. B. Coussens, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.*, **1999**, 1237-1241

[3] 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