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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:** Development and application of Energy Dispersive XAFS for Homogeneous Systems	**Experiment number**: CH1275
Beamline: ID24	**Date of experiment**: from: 2-8 July 2003, 26-02 Dec. 2003	**Date of report**: 01-09-2004
Shifts: 36	**Local contact(s)**: Dr. Steven Fiddy	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Drs. Moniek Tromp* Dept. Inorganic Chemistry and Catalysis, Utrecht University, NL
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Additional experimentalists: A.M.J. van der Eerden*, G. Mesu*, K. Kervinen*, University of Utrecht

Report:

The second part of this long term project has resulted in a full paper:

Titel paper: Multi-technique Approach to Reveal the Mechanism of Cu(II) Catalyzed Arylation Reactions : Introducing a Novel Time-Resolved EDXAFS/UV-Vis Set-up for Homogeneous Catalysis

Authors: Moniek Tromp, Sander S. van Berkel, Adri van den Hoogenband, Martinus C. Feiters, Bas de Bruin, Steven G. Fiddy, Jeroen A. van Bokhoven, Piet W. N. M. van Leeuwen, Diederik C. Koningsberger, Gino P. F. van Strijdonck

Submitted to *J. Am. Chem. Soc.*

Abstract

Multiple *in situ* and time-resolved spectroscopic techniques (EDXAFS, UV-Vis, EPR, NMR, XRD) are described to reveal detailed structural and electronic information on reaction intermediates of an important, anaerobic Cu(II) catalyzed N-arylation of imidazole. Based on these results, a novel mechanism for this Cu(II) catalyzed arylation reaction is proposed.

We have developed a novel set-up which enables the simultaneous acquisition of time-resolved *in situ* XAFS and UV-Vis data on homogeneous catalytic systems. A stopped-flow module is used to perform the reactions. Special cuvettes have been designed, in which the X-rays and UV-Vis light traverse perpendicular to one another. Different path lengths enable the simultaneous ED-XAFS and optical fibre UV-Vis experiments on the reaction mixture.

The N-arylation of imidazole was performed in a NMP/H_2O solvent mixture, at ambient temperature and atmosphere, using the commercially available Cu-catalyst $[Cu(OH)(TMEDA)]_2Cl_2$ (**I**). The system was

shown to be a good and effective catalyst. The reaction does not require the presence of dioxygen or a base. The presence of H_2O is however necessary for the reaction to proceed.

The spectroscopic study resulted in the characterization of several reaction intermediates. The first and selectivity determining step in the reaction is the reaction of the dimeric Cu(II) complex with imidazole, forming a monomeric Cu(II)(Imidazole) intermediate **II**. Upon subsequent addition of phenylboronic acid an Cu(III)(imidazolate)(phenyl) intermediate **III** is formed which after reductive elimination forms the phenylimidazole product and the Cu(I) monomeric species **IV** as characterized here. Finally, the Cu species is reoxidized forming back Cu(II) mononuclear and dinuclear complexes. Inhibition by imidazole and phenylimidazole is observed. The phenylboronic acid is, in combination with H_2O, involved in the oxidation and reoxidation steps in the described catalytic cycle.

In progress

Kinetic studies are in progress to model the spectroscopic ED-XAFS and UV-Vis results on Pd deactivation obtained as described in *Chem. Comm.* **2003**, 128-129 (see previous report) and the combined ED-XAFS/UV-Vis results on the above described Cu arylation reaction.

Publications resulting from the total long term project CH1275

M. Tromp, J.R.A. Sietsma, J.A. van Bokhoven, G.P.F. van Strijdonck, A.M.J. van der Eerden, P.W.N.M. van Leeuwen, D.C. Koningsberger, 'Deactivation Processes of Homogeneous Pd Catalysts using In Situ Time Resolved Spectroscopic Techniques', *Chem. Comm.* **2003**, 128-129.

M. Tromp, S. S. van Berkel, A. van den Hoogenband, M. C. Feiters, B. de Bruin, S. G. Fiddy, J. A. van Bokhoven, P. W. N. M. van Leeuwen, G. P. F. van Strijdonck, D.C. Koningsberger, 'Multi-technique Approach to Reveal the Mechanism of Cu(II) Catalyzed Arylation Reactions: Introducing a Novel Time-Resolved ED-XAFS/UV-Vis set-up for Homogeneous Catalysis', submitted to *J. Am. Chem. Soc*.

M. Tromp, 'Developments of Time-Resolved XAFS Spectroscopy Techniques – Applications in Homogeneous Catalysis', PhD thesis **2004**, Utrecht University, the Netherlands.

G. Rothenberg, M. Tromp, G.P.F. van Strijdonk, 'Detailed Mechanistic Studies on the Deactivation of Homogeneous Pd Complexes using In Situ Spectroscopic Techniques', in preparation.

G. Rothenberg, M. Tromp, G.P.F. van Strijdonck, 'Mechanistic Studies on Cu(II) Catalyzed Arylation Reactions', in preparation.