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:** X-Ray Absorption Studies on Palladium Ligand Complexes for Allylic Alkylation Reactions	**Experiment number**: CH-1085
Beamline: BM29	**Date of experiment**: from: 28/05/01 7:00hr to: 01/06/01 7:00hr	**Date of report**: 19/02/2002 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Dr. Stuart Ansell	

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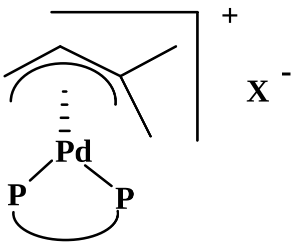
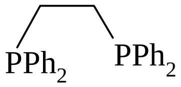
Report:

The use of bidentate diphosphine ligands shows excellent results in important palladium catalyzed reactions as the amination of aryl halides [1a] and the allylic alkylation [1b]. Both the steric and electronic properties of the catalyst can be altered by these bidentate ligands, as a result of their rigid coordination to the metal center. This implies that for bidentate ligands, also the P-Pd-P angle (bite angle) is an important ligand parameter. Recently, we have developed an interesting series of ligands based on a xanthene backbone, that enforce a wide bite angle [2].

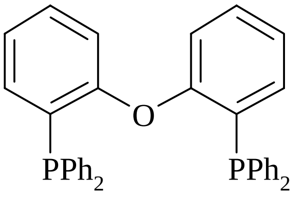
(allyl)Pd(ligand) complex



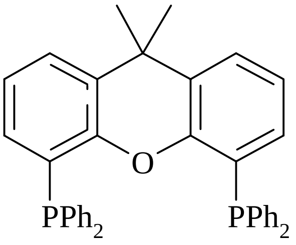
Ligands:



dppe



DPEphos



Xantphos

The catalytic allyl reaction intermediates could be isolated and they were also investigated with molecular modeling, X-ray crystallography and NMR techniques [3]. It is, however, using these techniques not possible to investigate the catalyst in solution. The value of the bite angle of the ligand in reaction medium cannot be determined by NMR and simulating the solution behavior of the complexes by modeling techniques requires much time and no reference data are known. Bidentate diphosphine palladium catalysts with a coordinated allyl moiety, (P-P ligand)Pd(allyl), are measured with EXAFS in both solid state and solution.

XAFS measurements of the catalyst in solution provide vital information about the catalytic active (precursor) species. XANES and EXAFS analysis yield the electronic structure and the geometry of the catalytic active species in the solution. This information is essential for the understanding of the catalytic behavior of the different Pd-ligand complexes. Furthermore, the obtained structures enable us to perform an Energy Dispersive EXAFS investigation on the catalyst during the allylic alkylation reaction and help us interpreting the obtained Energy Dispersive EXAFS data.

The different (allyl)Pd(P-P ligand) complexes are measured with different allyl moieties, C_3H_5 and C_5H_9, and with the different counterions Cl^- and BF_4^-. The complexes are solubilized in acetone and THF in which the allylic alkylation reaction can be carried out.

The EXAFS spectra of the known (allyl)Pd(ligand) complexes are compared with their solid state crystal structures and a good reproduction of the crystal structures is obtained. Subsequently the geometrical parameters in solution are determined. It is observed that the Pd(P-P ligand) catalyst structures itself do not change upon dissolution, only the disorder is increasing (increasing felixibility). However, the coordination of the allyl moiety is clearly dependent of the P-P ligand and the solvent, which already hints to the differences observed in reaction selectivity in the allylic alkylation reaction.

NMR studies of the isolated complexes indicate that the counterion of the cationic complexes may coordinate to the palladium center, thereby possibly influencing the geometry of the catalyst. NMR techniques however, cannot be used to estimate the average distance of the counterion to palladium and its effect on the geometry of the complex. The EXAFS results do not show a Pd-Cl or Pd-BF_4 coordination at distances below 4 Å, so any influence for catalysis will be small.

Determination of the P-Pd-P bite angle of the complexes in solution is still in progress. Therefore, also modeling studies have to be done to understand and interpret the XANES spectra of the complexes in detail.

References:

[1] 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

[2] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Pure & Appl. Chem.*, **1999**, *71*, 1443-1452

[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*, 3363-3372