EUROPEAN SYNCHROTRON RADIATION FACILITY

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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:**

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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

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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.

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Our group has discovered that $Pd(OAc)_2$ can catalyze Suzuki-Miyaura (SM) biaryl coupling reactions at room temperature without using any additives.[1] We observed that the presence of water is crucial for the success of this reaction. The goal is to identify the activation and deactivation/decomposition of the Pd catalyst in solution, particularly in the presence of different solvents, reactants and additives by means of the stopped-flow/UV-Vis/Energy Dispersive EXAFS facility of ID24.

Reactions examined:

1. Structure of $Pd(OAc)_2$ in solution. Although the solid state structure of $Pd(OAc)_2$ has been long established to be trimeric (bridging acetate ligands),[2] there is some controversy surrounding the solution structure of $Pd(OAc)_2$. An earlier QEXAFS study suggests that a solution in NMP assume a monomeric structure[3], whereas a recent NMR study revealed that the trimeric structure may be retained in solutions of methanol, chloroform and benzene (Scheme 1).[4] To probe whether the polarity of solvent can cause substantial dissociation into monomers, the EXAFS spectrum of $Pd(OAc)_2$ is recorded in toluene and DMF – the two most common solvents used in SM reactions. The spectra will be re-examined for any Pd....Pd contacts.
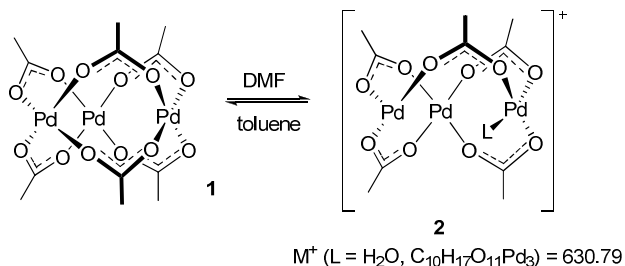
Scheme 1. Solution structures of Pd(OAc)₂.

M⁺ (L = H₂O, C₁₀H₁₇O₁₁Pd₃) = 630.79

From **Figure 1 (ii)** the differences between the reference sample in powdered form, which represents the trimeric structure, and the solutions of Pd acetate in toluene and DMF measured on ID24 can be qualitatively observed. The toluene solution appears to be structurally closer to the reference sample than the DMF one.

EXAFS analysis of this set of data has allowed us to find that both toluene and DMF solutions are in equilibrium between a trimeric and a monomeric structure of the Pd acetate under the experimental working conditions (conc. ≥ 40 mM, T = 25°C). In the case of the toluene solution this equilibrium is strongly shifted towards the trimeric model. Surprisingly, the more polar DMF solution has also a higher contribution of the timeric model, although the monomeric structure is present in higher degree than in the toluene case. A quantitative multiple component analysis (MCA) is currently underway to asses the percentage of each of these models contributing to the experimental data.

As an example, in **Figure 1 (ii)** is shown the fitted trimeric model to the toluene Pd aceate solution. The following structural parameters were found using the program Viper[5], where N=coordination number, R=interatomic distance, σ^2=Debye-Waller factor, R-factor=goodness of the fit in Viper:

Pd–O			Pd–C			Pd–Pd			R-factor
N	R(Å)	σ^2	N	R(Å)	σ^2	N	R(Å)	σ^2	
4	1.995(5)	0.003(1)	4	2.917(23)	0.002(4)	4	3.231(84)	0.029(30)	21
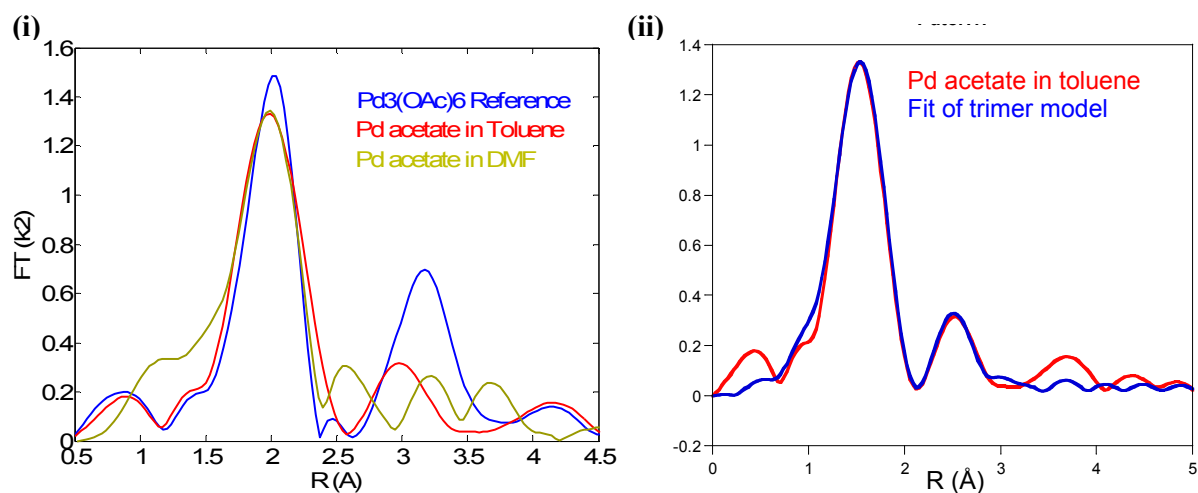
Figure 1. (i) Comparison between the FT as a function of interatomic distance of the Pd acetate reference spectrum (blue line), Pd acetate in toluene (red line) and Pd acetate in DMF (green line). **(ii)** Fitted Pd acetate trimeric model (in R-space) to the toluene solution of Pd acetate. The x axis of these figures represents the interatomic distance (R) in Å, and the y axis the Fourier Transform as a function of k.

2. Addition of arylboronic acid to Pd(OAc)$_2$ and subsequent oxidative addition reaction. Addition of two equivalents of ArB(OH)$_2$ to a solution of Pd(OAc)$_2$ in anhydrous DMF led to immediate decomposition to Pd black. Interestingly, the process was retarded in the presence of water and inorganic base (K$_3$PO$_4$). This suggest that these additives are able to stabilize the Pd(II) precursor.

When two equivalents of arylboronic acid was added to a solution of Pd(OAc)$_2$ in the presence of 5 equivalents of ArBr, the decomposition of Pd can be intercepted by the formation of a new Pd(II) species, observed as an orange solution. EXAFS suggests the formation of a Pd-Br bond (to be confirmed by MS), indicating that oxidative addition has taken place. Thus, we have proven that the oxidative addition of aryl bromides to unligated Pd(OAc)$_2$ can indeed occur under ambient conditions. Furthermore, that the generation of a catalytic active species and decomposition share a common intermediate (**Scheme 2**).
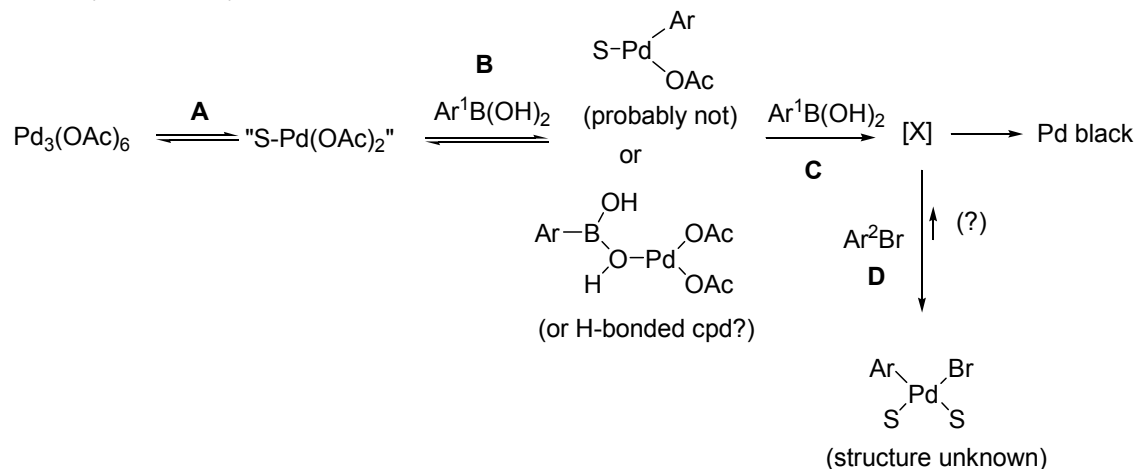
Scheme 2. Suggested pathways of generation of catalytic active species/decomposition product from Pd(OAc)$_2$.

Further experiments were also conducted to examine the effect of certain additives such as oxidants (peroxide) and organic base (triethylamine). The former was found not to inhibit the decomposition of Pd. However, the formation of a dimeric Pd-Br compound **3** (**Figure 2**) may be observed.
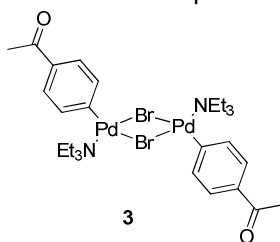
Figure 2.

Work is currently underway to analyse the results in depth, and we project that a publication will be produced in 2008, with a possible further publication in 2009.

References:
[1] "A Practical and General Synthesis of Unsymmetrical Terphenyls by Tandem Suzuki-Miyaura Coupling Reactions", J. M. A. Miguez, L. A. Adrio, A. Sousa-Pedrares, J. M. Vila, and K. K. Hii*, J. Org. Chem., 2007, 72, 7771-7774.
[2] A. C. Skapski, M. L. Smart, J. Chem. Soc. D, Chem. Commun., 1970, 658.
[3] J. Evans, L. O'Neill, V. L. Kambhampati, G. Rayner, S. Turin, A. Genge, A. J. Dent, T. Neisius, J. Chem. Soc., Dalton Trans. 2002, 2207.
[4] V. I. Bakhmutov, J. F. Berry, F. A. Cotton, S. Ibragimov, C. A. Murillo, Dalton Trans., 2005, 1989.
[5] K. V. Klementiev, VIPER for Windows, freeware: www.desy.de/~klmn/viper.html; K.V.Klementev, J. Phys. D: Appl. Phys, 2001, 34, 209.