

**Experiment title:**

Time resolved EDE studies of homogeneous palladium catalysts for carbon-carbon bond forming reactions

**Experiment number:**

CH-632

**Beamline:**

ID24

**Date of experiment:**

from: 10 May 1999 to: 15 May 1999

**Date of report:**

2 September, 1999

**Shifts:**

12

**Local contact(s):**

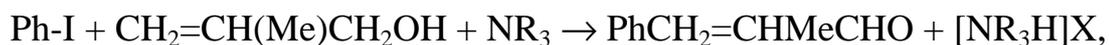
Dr S Diaz Moreno

*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):****P Bolton\*** Department of Chemistry, University of Southampton, UK**J Evans\*****L O'Neill\*****G Rayner\*****A J Dent\*** CLRC Daresbury Laboratory, UK**Report:**

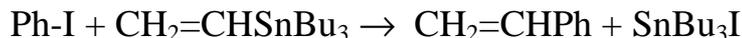
Energy dispersive EXAFS (EDE) at the Pd K-edge was used to investigate the structures of the palladium complexes present in three catalyst systems for C-C coupling:

- i) A highly efficient catalyst for the Heck reaction based on palladacycle complexes of the type  $[\text{Pd}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(o\text{-tolyl})_2(\mu\text{-X}))_2]$  reported by Herrmann.<sup>1,2</sup> and
- ii) A Stille coupling<sup>3</sup> using  $\text{AsPh}_3$  as the promoting ligand.
- iii) A methanol carbonylation catalyst system based on with an iodide co-catalyst.<sup>4</sup>

The first two experiments utilised an ambient pressure, variable temperature solution cell, using concentrations in the range 30 – 60 mM Pd. The formation of the catalyst was monitored and then the temperature elevated to monitor the structure of the complexes during the period of catalysis (1 hr). Spectra of good quality were obtainable with 100 accumulations and detector exposure times of *ca* 1 – 5 ms. Data analysis is still underway. However, this has shown that the Herrmann palladacycle ( $\text{X} = \text{OAc}$ ) can be partially characterised by analysis of the EDE data. The coordination sphere of 2 oxygens, 1 carbon and 1 phosphorus is best fitted to a two component model of phosphorus and oxygen. The formation of this palladacycle from the reaction of palladium acetate with  $\text{P}(o\text{-tolyl})_3$  appears to take place without any identifiable intermediate. Analysis of the *in situ* data on the following catalysed reaction is underway:

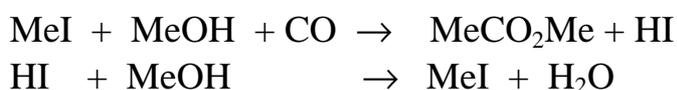


The Stille reaction investigated was:



$\text{Pd}_2(\text{dba})_3$  (dba = dibenzylideneacetone) was used as the precursor and the structures of the complexes formed with an active co-catalyst,  $\text{AsPh}_3$ , compared with that with two related ligands,  $\text{PPh}_3$  and  $\text{P}(\text{OPh})_3$ . A series of colour changes take place during catalysis, and it is hoped that analysis of the EDE results will indicate the nature of these changing complexes.

The third experiment was carried out in an elevated pressure cell, using 5 bar of CO and monitoring the Pd environments a up  $100^\circ\text{C}$ . Alignment of this cell proved to be difficult, and so further development is necessary. Nevertheless one variable temperature study was carried out under a CO pressure. The catalysed reaction is:



## References

1. W A Herrmann, C Brossmer, K Öfele, C P Reisinger, T Proermeier, M Beller and H Fischer, *Angew Chem Int Ed Engl*, 1995, **34**, 1844.
2. W A Herrmann, C Brossmer, C-P Reisinger, T H Riermeier, K Öfele, and M Beller, *Chem Eur J*, 1997, **3**, 1357
3. J K Stille, *Angew Chem Int Ed Engl*, 1986, **25**, 508.
4. J Yang, A Haynes and P M Maitlis, *Chem Commun*, 1999, 179.