



	<b>Experiment title:</b> Application of XAS to the characterisation of highly dilute transition metal homogeneous catalysts	<b>Experiment number:</b> CH962
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 3 <sup>rd</sup> May 2001                      to: 9 <sup>th</sup> May 2001	<b>Date of report:</b> 30 <sup>th</sup> August 2002
<b>Shifts:</b> 18	<b>Local contact(s):</b> Thomas Neisius	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

Prof. John Evans,\* Dr. Steven Fiddy,\* Dr. Mark Newton,\* Mr Graham Rayner\*  
Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

Prof. Richard Oldman  
ICI Technology, PO Box 8, The Heath, Runcorn, Cheshire WA7 4QD, UK

**Report:**

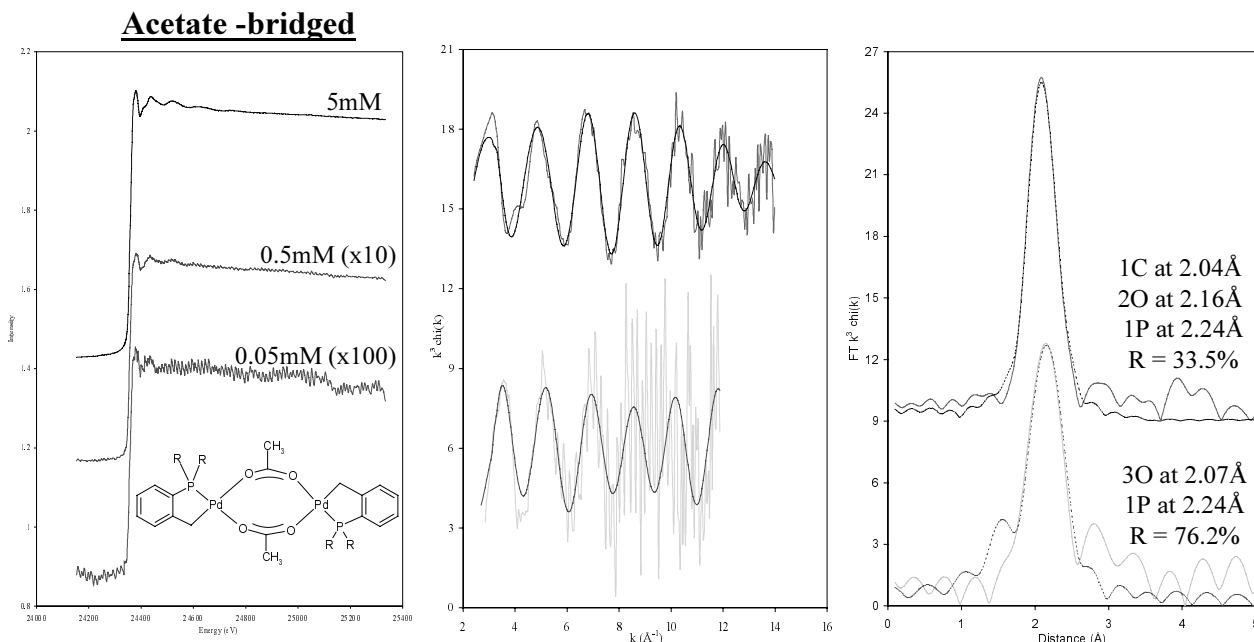
This beamtime had two main aims:

- 1) To identify the dilution limit of ID26 for palladium species.
- 2) To identify the major species in catalytic solution during the Heck C-C coupling reaction.

For the 1<sup>st</sup> aim, we need to answer three questions:

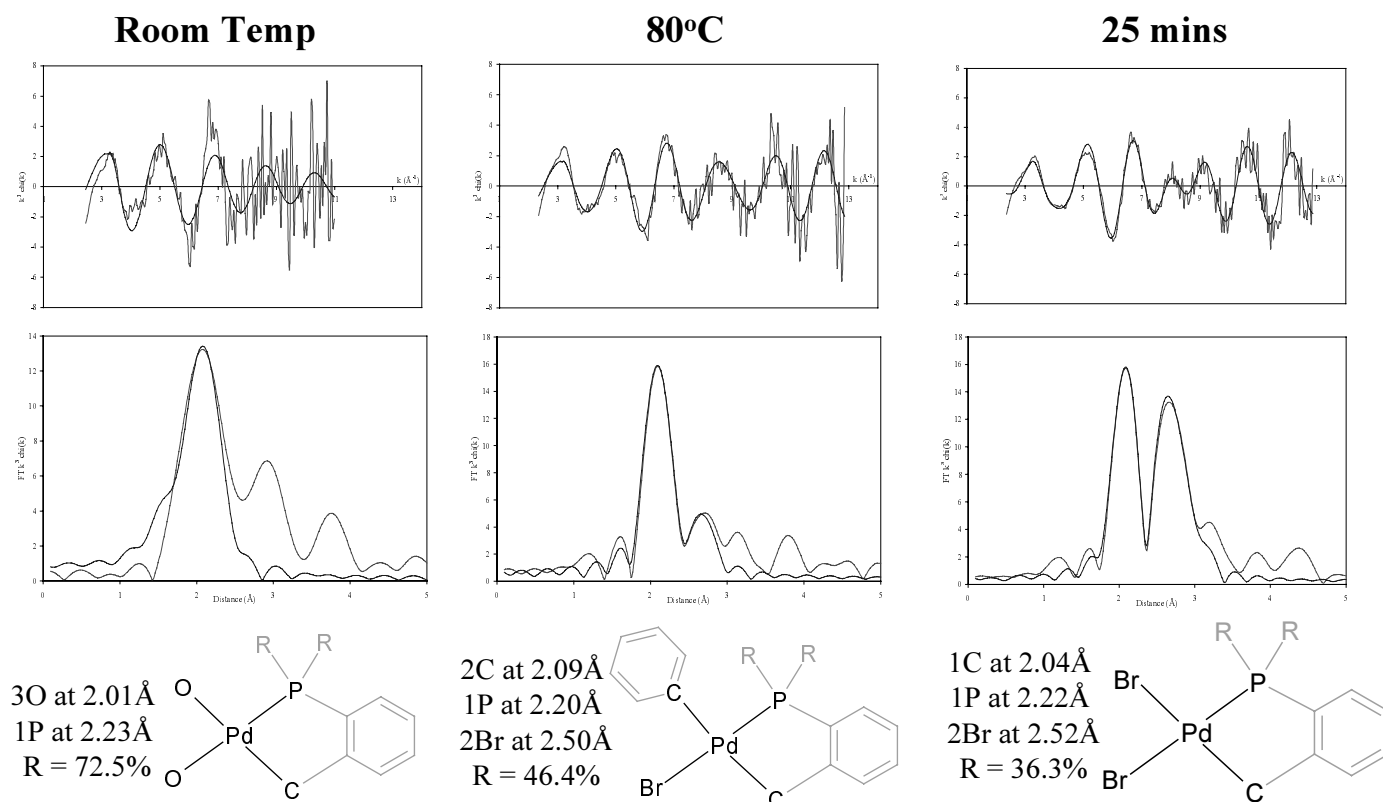
- a) What was the dilution limit of ID26 both investigating standard compounds of known molecular structure and under catalytic conditions?
- b) Over what time periods would it be possible to collect data of an analysable quality?
- c) Would the compounds we wanted to investigate be stable under the intense radiation of the beam and how would this be affected by changes in conc.?

Figure 1 shows a comparison of 3 different dilution levels for a palladacycle solution dissolved in NMP. Several palladium compounds were tested for dilution limits during the experiment - Pd(OAc)<sub>2</sub>, [Pd(PPh<sub>3</sub>)<sub>2</sub>(Ph)(I)] and a bromine analogue of the palladacycle. Importantly, at the time using a solid state detector, it was found that the dilution limit of ID26 on standard palladium compounds in a non-halogenated solvent is 0.5mM (50ppm). Each scan took approximately 30 minutes (6 were usually required to produce analysable data), therefore 3 hours were needed to produce good quality data. Finally and importantly, for these compounds at all concentrations, no obvious signs of decomposition to Pd metal could be observed either visually or during the EXAFS analysis.



**Figure 1: Dilution results for the acetopalladacycle (see structure inset) diluted in NMP.**

The 2<sup>nd</sup> aim was to identify palladium species in catalytic solution. In our first attempts, iodobenzene was used as the phenyl halide of choice. However, it became clear that the use of phenyl iodide was going to prove impossible as the iodide fluorescence was so intense compared with the palladium fluorescence that the palladium edge could not be observed, let alone analysed (For 5mM Pd, I to Pd molar ratio =250:1). Therefore, bromobenzene was used, along with the use of a Z-1 foil (Rh) to filter out as much of the bromine scatter as possible. Using this system, it was possible to produce high quality/resolution data with palladium concentrations of 5mM. Analysable data was achieved by four scans and therefore, approx. 2 hrs was needed for each sample.



**Figure 2: The variation in EXAFS and FT recorded at certain temperature/time intervals for the Heck reaction between bromobenzene and butyl acrylate catalysed by palladium acetopalladacycle (Pd concentration = 5mM/500ppm).**

For the acetopalladacycle catalysed system (figure 2), by EXAFS we are able to clearly observe that:-

- 1) the phosphorous and the o-tolyl C appear to remain bonded throughout the reaction. This is interesting as there is great debate as to whether the P-Pd and/or C-Pd bond break/reform during the course of the catalytic cycle.
- 2) oxidation addition of bromobenzene is again an initial stage of the reaction and occurs by a temp of 80°C. This is an important point as it has been hypothesised by Shaw et al (Chem. Comm., 1998, 1361) that the mechanism may also proceed via Pd(II)/Pd(IV) species, with the initial stage being the addition of the olefin to the Pd complex. The data collected is not consistent with this hypothesised mechanism and consequently, the Pd(0)/Pd(II) mechanism is favoured by us at this concentration level.
- 3) Finally, at the end of the reaction, a Pd species with similar structural properties to the Br palladacycle is observed.

**Most importantly from this beamtime, the formation of different species can be clearly observed and characterised, by EXAFS, during the course of the Heck reaction on station ID26 at the ESRF.**