



	Experiment title: Application of XAS to the determination of the characterisation of highly dilute transition metal homogeneous catalysis	Experiment number: CH1175
Beamline: ID26	Date of experiment: from: 26 th September 2001 to: 2 nd October 2001	Date of report: 30 th August 2002
Shifts: 18	Local contact(s): 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.

Dr. Robert Tooze

ICI-Synetix, PO Box 1, Belasis Avenue, Billingham, TS23 1BL, UK.

Report:

Firstly, the installation of a new Ge-element solid state fluorescence detector was conducted. This provided much better resolution and an improvement in signal collection, providing better quality data and allowing a small drop in concentration level to 2mM (c.f. CH962, where minimum concentration. in catalytic solution was 5mM). However, this took several days of beamtime and so the amount of samples that could be characterised was restricted. Nevertheless, important results were obtained and new information about the beamline and the catalysts themselves could be gathered.

The aim of this beamtime were two fold. Firstly, the acetopalladacycle catalysed Heck reaction was studied in further detail and at lower dilution levels. There is considerable debate as to the reaction mechanism via which this catalysts proceeds. At high concentration levels, the dimer species tend to persist, however it is hypothesised that as the concentration level is reduced, a more active monomer species predominates, leading to increased catalytic activity. It was found that even at a concentration level of 2mM Pd, the major species formed over time during the catalytic cycle of the Heck reaction were very similar to that which had been observed previously for the same reaction at 5mM (see experimental report CH962). The initial starting EXAFS indicates that there are no obvious changes in structure, with the data fitting to a model based on the crystal model of the acetopalladacycle (figure 1). Importantly at this stage, no features could be associated with a Pd...Pd distance indicating dimerisation. However, this is also the case at high concentrations, and therefore ideas are being discussed to attempt to optimise the ability to visualise the longer range palladium shell by EXAFS. This has been an important feature to emerge from the present work. At 80°C, a change in the EXAFS occurs, and the data can be best fitted to a model containing a bromine atom. This is important as it suggests that oxidative addition of the bromobenzene has taken place and is, consequently, an initial stage in the Heck reaction. Finally after the entire reaction has reached completion, the final species can be best fitted to a model representing the bromine bridged acetopalladacycle. These results will be used to compare with the EDEXAFS data collected previously on ID24 and published in the future.

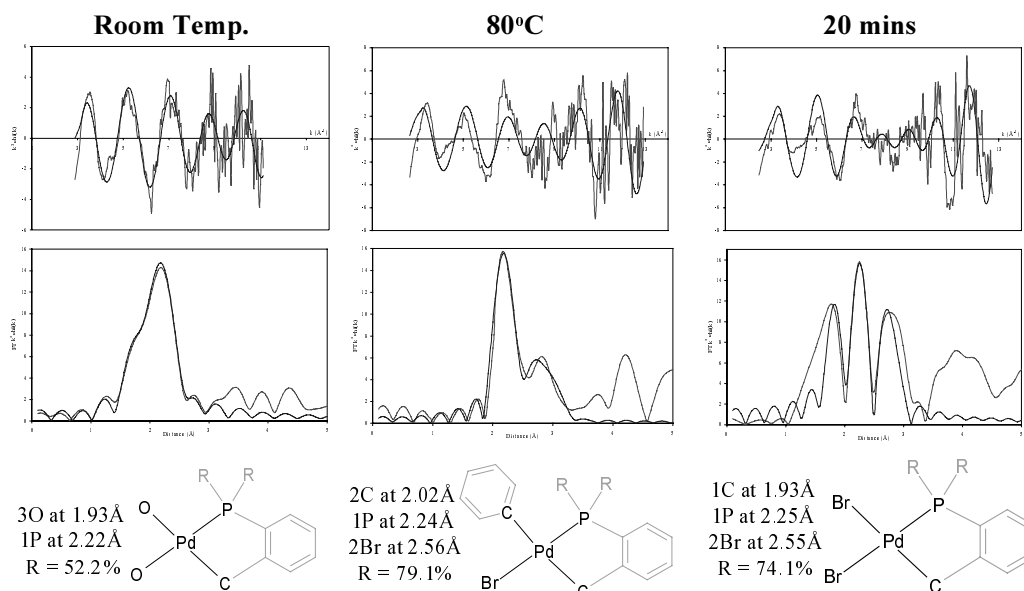


Figure 1: EXAFS and FT recored at certain temp./time intervals during the course of the Heck reaction catalysed by palladium acetopalladacycle catalysts (Pd concentration = 2mM/208ppm).

Secondly, a novel class of catalysts were also investigated to discover whether they would be suitable for study by EXAFS and how their reaction mechanism compared with that of the acetopalladacycle catalysts. The catalysts unusually utilises a carbene as a strongly held auxiliary ligand and an imidazole nitrogen as the potentially labile donor. They form active Heck catalysts at very low concentrations (10^{-2} - 10^{-5} mol %), too low for NMR studies. Importantly, this was the first attempt to study these catalysts by EXAFS. Initially standard dilution studies were conducted on these catalysts to discover the effect of dilution for these catalysts. These catalysts did not produce any signs of palladium deposition, making them suitable for EXAFS studies and up to a 5mM level, produced EXAFS that was very similar with single crystal data for these carbene complexes and standard EXAFS studies of the catalysts in their solid forms. However, further dilution to the catalytic concentration levels could not be performed, but a continuation of dilution studies to diluter levels should provide potential clues as to why these catalysts are active at low concentrations.

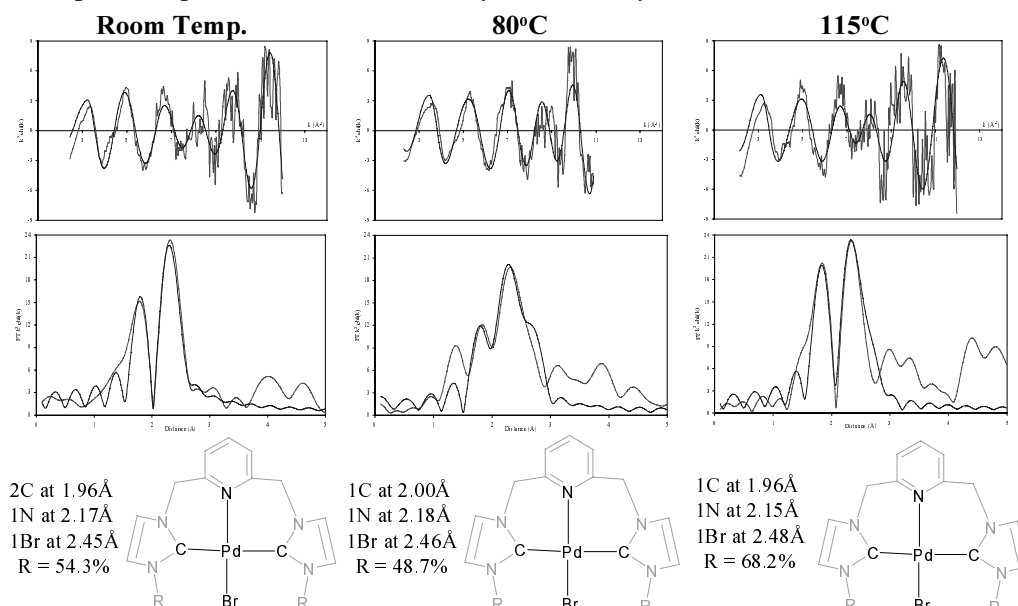


Figure 2: EXAFS and FT recored at certain temperature intervals during the course of the Heck reaction catalysed by palladium pincer carbene catalysts (Pd concentration = 2mM/208ppm).

The major species observed during the cycle of the carbene Heck catalysts were also characterised. Interestingly, for the pincer carbene catalysts (figure 2), a clear change from Cl to Br could be observed at room temperature, suggesting either substitution or oxidative addition of the Br from bromobenzene taking place. However, further studies of these catalysts are important to confirm and characterise these systems thoroughly.