	Experiment title: **Time Resolved Energy Dispersive EXAFS Studies of Heterogeneous Catalysts**	**Experiment number**: **CH864**
Beamline: ID24	**Date of experiment**: from: 31 May 2000 to: 6 June 2000	**Date of report**: 12 March 01 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: S Diaz Moreno	

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Report:

Energy dispersive EXAFS (EDE) (Pd K edge) was used to monitor the changes in the palladium coordination site during the activation and operation of catalysts for the Heck reaction involving the coupling the aryl group in iodobenzene with an alkene, 2-methylprop-1-en-3-ol. The catalyst studied was that due to Herrmann *et al.*, in which a

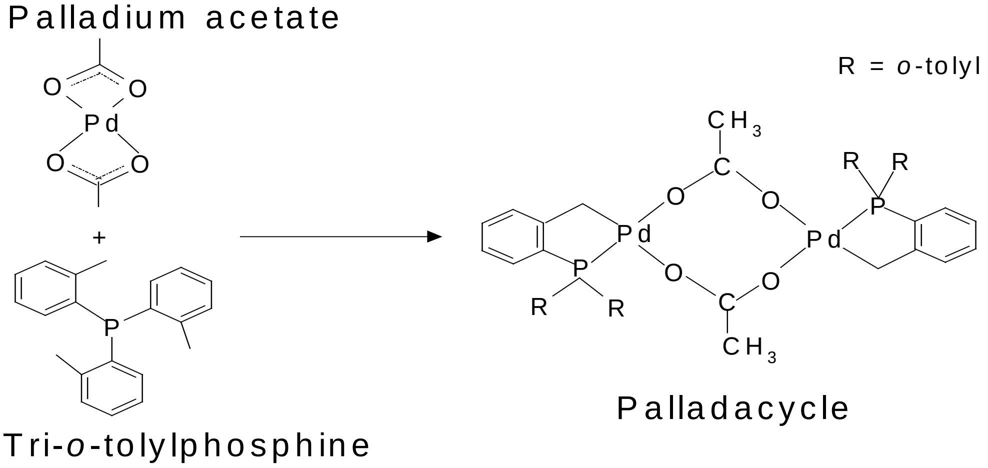

Figure 1: *The formation of the Herrmann palladacyle*

palladacycle is formed by cyclopalladation of coordinated *tri*(*o*-tolyl)phosphine, as shown in Figure 1.[1]

This reaction was monitored using the white line intensity, which is reduced on going from palladium actetate to the product. Analysis of the EDE data is consistent with this reaction.

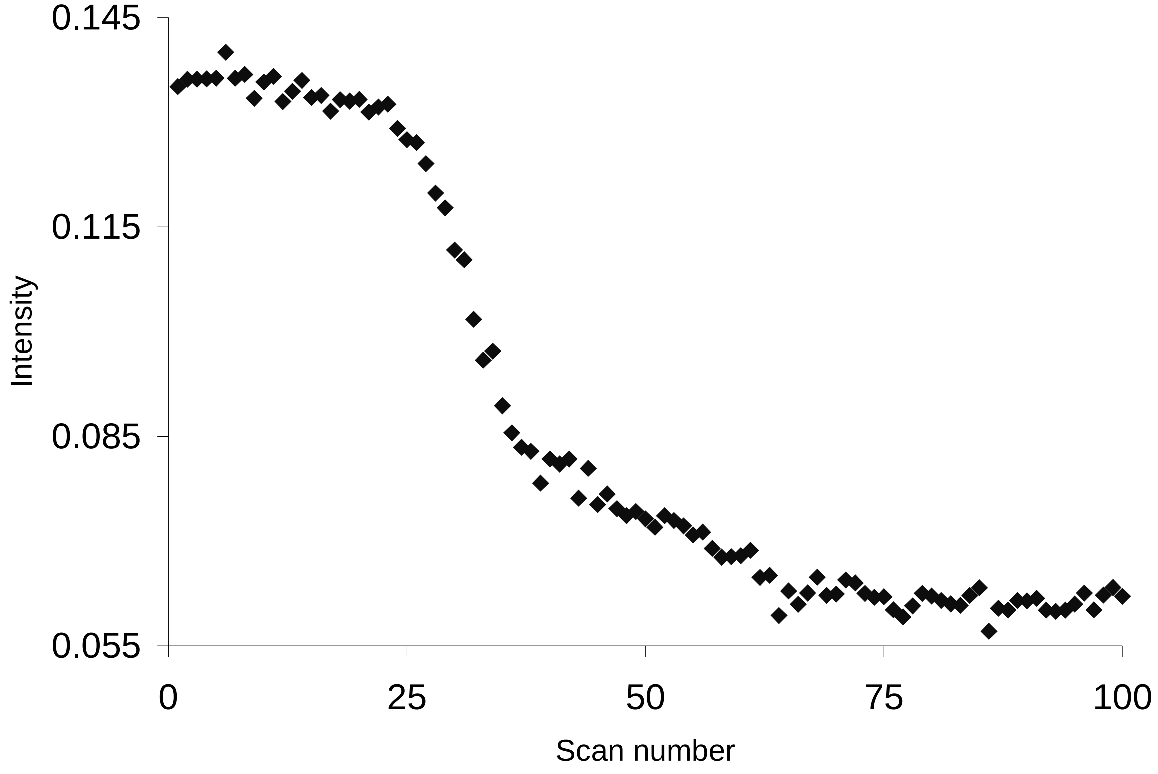

Figure 2: *Changes in the normalised white line intensity near the Pd K-edge over the time for the reaction of* $Pd(OAc)_2$ *with* $P(o\text{-tolyl})_3$ *(1:3) during a temperature ramp to 130°C. Conditions: Plot 10: 0 min, 27°C; 50: 16 min, 106°C; 62: 21 min, 130°C; 99: 36 min, 130°C*

On carrying out the Heck reaction (with NBu_3 as the base to neutralise the HI also formed, and NMP as solvent), changes in the coordination ligand set can be observed. The final form of the catalyst appears to be the iodo, rather than the acetato bridged dimer. This is reflected in the changes in the Fourier transforms derived from spectra recorded during the course of this reaction (Figure 3).

The iodide ligand results for the oxidative addition of the iodobenzene, the phenyl group being subsequently coupled with the 2-methylprop-1-en-3-ol, resulting in 1-phenyl-2-methylpropanal.

Interestingly, when the catalysis is carried out using $Pd(OAc)_2$ and $P(o\text{-tolyl})_3$, rather than the preformed acetate-bridged palladacycle, this complex is not present during catalysis. Instead a mixture of three similar palladium complexes is evident by ^{31}P NMR. This demonstrates the merit of presynthesis for catalyst formation.

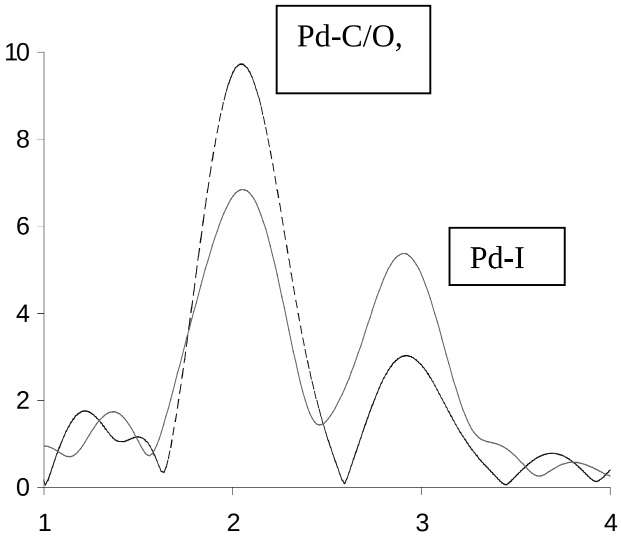

Figure 3: *Fourier transforms of Pd K-edge EDE spectra of the Herrmann catalyst for the Heck reaction (……) at the start and (——)at the end of the reaction (2h at 130°C).*

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.