

**Experiment title:**

Energy-dispersive EXAFS studies of homogeneous transition metal catalysts

Experiment number:

CH449

Beamline:

ID24

Date of experiment:

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15

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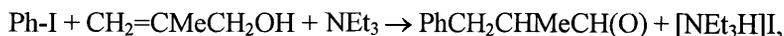
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Report:

Two types of time resolved experiments were carried out, both using a Laue monochromator to probe the palladium K-edge by energy dispersive EXAFS (EDE). The analysis of these results was delayed due to problems in converting data into ASCII from the non-standard form produced by the CCD-detector control computer. Once this had been overcome, a significant fraction of the results displayed "phantom" EXAFS, due to the difficulty in obtaining the same effective background for the sample and normalisation spectra. It is hoped that the new beam-position feedback systems to be installed in autumn 1998 will alleviate this problem.

The first chemical challenge was to investigate the reaction between $[\text{Pd}(\text{N-N})\text{Cl}_2]/\text{AgBF}_4$ and $\text{AlEt}_2(\text{OEt})$ using an ambient temperature stopped flow cell. Previous work had employed a relatively small pathlength (ca 3 mm) at the Ni K-edge, to keep the mixing time as low as possible. However, the lower absorption and edge jump at the Pd K-edge requires a longer pathlength (ca 20 mm) therefore the cell volume and dead time are increased. The results show that there is rapid alkylation of the palladium centre by the aluminium reagent. The best data was obtained for $\text{N-N} = \text{NMe}_2\text{CH}_2\text{CH}_2\text{NMe}_2$.

In the second problem, an elevated temperature solution cell (pathlength reduced to 5 mm to offset absorption due to the iodobenzene, temperatures up to 115°C) was utilised to monitor the catalyst formation and operation for several Heck reactions for carbon-carbon bond formation,



with $[\text{Pd}(\text{OAc})_2]_3$ as the catalyst precursor, for the reaction between iodobenzene and 2-methallyl alcohol (with and without PPh_3 as a co-catalyst) in NMP (N-methylpyrrolidinone) solution. The results in the presence of PPh_3 are in contradiction of previous descriptions of the coordination centre after mixing at room temperature as being $\text{Pd}(\text{Ph})(\text{OAc})(\text{PPh}_3)_2$, since clear backscattering due to coordinated iodine is observed in what may be $\text{Pd}(\text{Ph})\text{I}(\text{PPh}_3)_2$. In the presence of PPh_3 , prior to catalysis, the palladium may be extracted as $[(\text{Ph})(\text{PPh}_3)\text{Pd}(\mu\text{-I})_2\text{Pd}(\text{Ph})(\text{PPh}_3)]$. On dissolution at 115°C a new species is present as the catalysis begins with a coordination sphere consistent with $\text{PdI}_2(\text{PPh}_3)(\text{alkene})$. During catalysis, this is steadily converted to $[\text{I}(\text{PPh}_3)\text{Pd}(\mu\text{-I})_2\text{PdI}(\text{PPh}_3)]$ as the iodobenzene is consumed.

In the absence of PPh_3 , it was shown that the 2-methallyl alcohol is necessary for any reaction to begin; on addition of this substrate, the ammonium salt of $[\text{I}_2\text{Pd}(\mu\text{-I})_2\text{PdI}_2]^{2-}$ is formed at room temperature. The iodide coordination number decreases as the temperature is raised to 50°C, and on reaching the catalysis temperature (70°C), the coordination sphere may be best fitted as consisting of 2 iodines and 2 carbons. Attempts to isolate the solution species by crystallisation failed as $(\text{NEt}_3\text{H})_2[\text{Pd}_2\text{I}_6]$ is precipitated both before and after catalysis. Hence the EDE results provide a better picture of the solution phase species.