

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Cr K edge XAFS characterisation of homogeneous catalysts for the selective tri- and tetra-merisation of ethene.	<b>Experiment number:</b> CH-2209
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 11 May 2005 to: 15 May 2006	<b>Date of report:</b> 30 Aug 2006
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr Sergey Nikitenko	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> John EVANS,* Jerome MOULIN,* Gillian REID,* Moniek TROMP* School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK		

## Report:

The programme outlined in the report for experiment CH-2125 was extended to include a detailed study of the solution species obtained during the activation of complexes of the type  $\text{CrCl}_3(\text{L}_3)$  by  $\text{AlMe}_3$ . This reaction models the procedure adopted for screening the catalytic activity for the conversion of ethene to higher alkenes. In those experiments the activating reagent was the partially hydrolysed material methylaluminoxane (MAO). An excess of  $\text{AlMe}_3$  chosen was that required to convert all of the precursor complex into a new species, as judged by UV-Visible and EPR spectroscopies.

For the complex  $[\text{CrCl}_3\{\text{S}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2\}]$ , which afforded activity for ethene oligomerisation, the analysis of the EXAFS data could best be fitted to a coordination sphere dominated by light atoms (3.0(2) carbon atoms; Cr-C 2.07(7) Å). A small feature in the Fourier transform (Figure 1) could be refined to a small contribution of Cr-S (0.3(3) with Cr-S 2.44 (5) Å. This suggests that the tridentate ligand is substantially lost after treatment with the aluminium reagent. Similar spectra and catalytic activity were observed for a series of open chain and cyclic tridentate ligands.

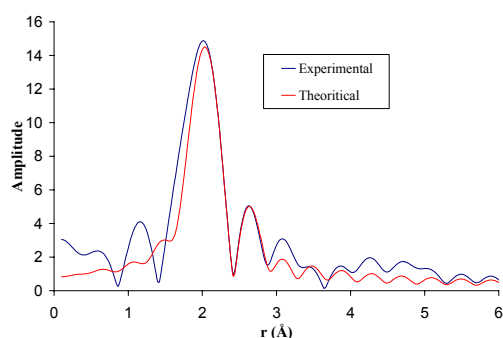


Figure 1. Fourier transform of the Cr K-edge EXAFS of  $[\text{CrCl}_3\{\text{S}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2\}] + \text{AlMe}_3$  in toluene.

However, the complex  $[\text{CrCl}_3\{\text{NH}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2\}]$  and related complexes provided selective catalysts for ethene trimerisation to hex-1-ene.<sup>1</sup> In this case (Figure 2), a higher total coordination was apparent,

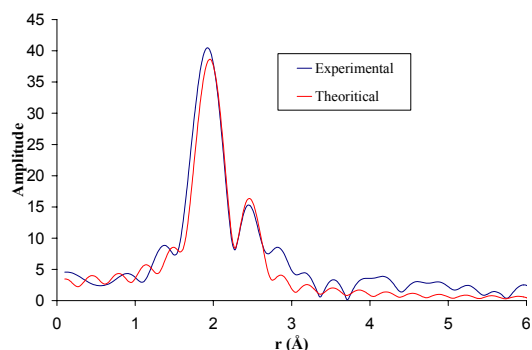


Figure 2. Fourier transform of the Cr K-edge EXAFS of  $[\text{CrCl}_3\{\text{NH}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2\}] + \text{AlMe}_3$  in toluene.

Atom	C.N.	R / Å	$2\sigma^2 / \text{\AA}^2$
C / N	4.0(2)	2.03(9)	0.008(4)
S	0.8(5)	2.37(8)	0.010(8)

and this is consistent with the replacement of all Cr-Cl bonds by methyl groups, as observed in the S-S-S-ligand, but also there is evidence for the retention of the Cr-N bond and the maintenance of one of the Cr-S links. The presence of strong bases is known to deprotonate the central nitrogen of the ligand, resulting in a stable Cr=N link. Probably this anchors the ligand which is also coordinated by one of the two sulfur arms.

Finally ligands of the type  $\text{NR}(\text{PPh}_2)_2$  can be utilised to afford tetramerisation catalysts, and this was modelled by the reaction of  $[\text{CrCl}_3\{\text{NPr}(\text{PPh}_2)_2\}(\text{THF})]$  with  $\text{AlMe}_3$ . Here the local scattering at the Cr

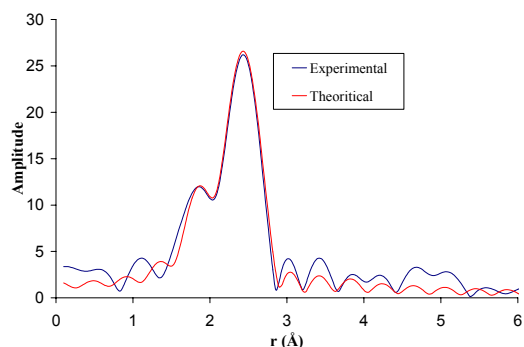


Figure 3. Fourier transform of the Cr K-edge EXAFS of  $[\text{CrCl}_3\{\text{NPr}(\text{PPh}_2)_2\}(\text{THF})] + \text{AlMe}_3$  in toluene.

is dominated by scattering from phosphorus atoms  $\{1.9(2) \text{ Cr-P at } 2.46(3) \text{ \AA}\}$  demonstrating the retention of the bidentate ligand. It is again clear that all Cr-Cl bonds have been lost in the activation process, with a small contribution of light elements to the back scattering ( $0.7(4) \text{ O/C at } 2.03(9) \text{ \AA}$ ).

These results show that these related complexes behave rather differently during activation by aluminium alkyls, and this may be the basis of their differing activity and selectivity for the catalytic catenation of ethene.

## References:

1. D.S. McGuinness, D.B. Brown, R.P. Tooze, F.M. Hess, J.T. Dixon, and A.M.Z. Slawin, *Organometallics*, 2006, **25**, 3605.
2. M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, and D. H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723.