Selective trimerisation of ethylene to 1-hexene with chromium or titanium based catalysts has become an important industrial process.\(^1\) While a metallacyclic mechanism has become generally accepted many details on the active species are still controversial. Analogous selective trimerisation of \(\alpha\)-olefins gives a range of isomeric trimer products suitable for mechanistic studies unavailable to ethylene trimerisation.\(^2\) However, most selective ethylene trimerisation catalysts are unable to trimerise \(\alpha\)-olefins and following our initial description of an active system based on triazacyclohexane complexes of CrCl\(_3\) in 2000\(^2\) no better catalysts have been reported until recently with activities of a few hundred turnovers.\(^3\) We have now optimised the catalysis using triazacyclohexane complexes to achieve reliable selective \(\alpha\)-olefin trimerisation at up to 5000 turnovers over a few hours.\(^4\)

We found that mainly the isomers shown above are formed and their ratio depends significantly on the N-substituents used in the triazacyclohexane ligand. Comparison of the GC-MS and \(^{13}\)C NMR spectra along with isotope labelling studies has now allowed us to identify and quantify all isomers (>1%) with their complete \(^{13}\)C NMR spectra for the trimer of 1-hexene and some other \(\alpha\)-olefins.

Selectively deuterium labelled \(\alpha\)-olefins show significant effects on the isomer ratios observed indicating the important role for H-transfer steps in the selectivity for some isomers. The results will be discussed with some DFT computational studies.