

Selectivity in trimerization of α -olefins

Randolf D. Köhn

University of Bath, UK

29 de Abril de 2016

12:00

Salón de Actos de Matemáticas (Facultad de Ciencias B)



CICLO CONFERENCIAS ISQCH 2016

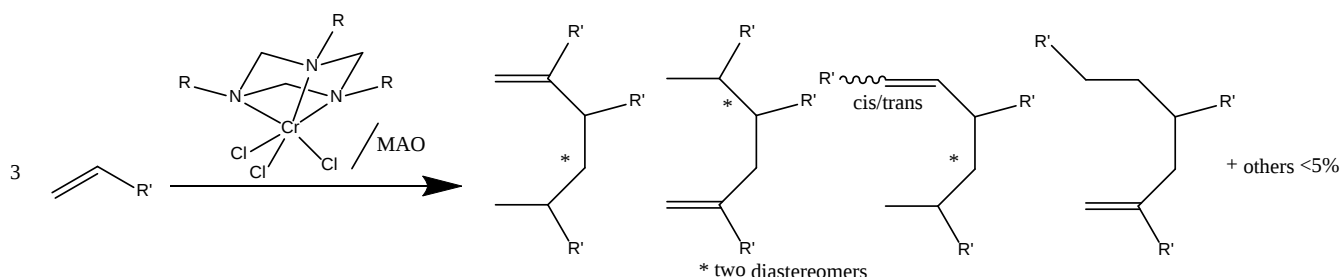
Selectivity in trimerization of α -olefins

R. D. Köhn, A. G. N. Coxon and G. Kociok-Köhn

University of Bath, Bath, United Kingdom

r.d.kohn@bath.ac.uk, http://www.bath.ac.uk/chemistry/contacts/academics/randolf_kohn/

Selective trimerization 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 trimerization of α -olefins gives a range of isomeric trimer products suitable for mechanistic studies unavailable to ethylene trimerization. However, most selective ethylene trimerization catalysts are unable to trimerize α -olefins and following our initial description of an active system based on triazacyclohexane complexes of CrCl_3 in 2000² no better catalysts have been reported until recently with activities of a few hundred turnovers.³ We have now optimized the catalysis using triazacyclohexane complexes to achieve reliable selective α -olefin trimerization 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 α -olefins.

Selectively deuterium labelled α -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 to rationalise the selectivity for the isomers.

1. D. S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321-2341
2. R. D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, *Angew. Chem.*, **112** (2000) 4519-4521; *Angew. Chem., Int. Ed. Engl.*, **39** (2000) 4337-4339
3. A. Sattler, J. A. Labinger, J. E. Bercaw, *Organometallics*, 2013, **32**, 6899-6902
4. A. G. N. Coxon, R. D. Kohn, *ACS Catal.*, 2016, **6**, 3008-3016.

CV:

1981 – 1989

Study of Chemistry at

Technischen Universität (TU) Berlin

Vordiplom 1983, Diplom 1986, Promotion 1989 under Prof. H. Schumann on *Darstellung und paramagnetische NMR-Untersuchung neuer Lanthanoid-Sandwich Komplexe*

25. October 1996

Habilitation at TU Berlin on *Übergangsmetallkomplexe - mit Triazacyclohexanen und Orthoamiden*; assessors: Prof. H. Schumann, Prof. K. Wieghardt, Prof. H. Brintzinger
Lecture: *Nitrogenase - die Suche nach Modellsystemen*

Professional career:

1997 – 1999

Privatdozent at TU Berlin

since 1. Oct. 1999 Lecturer in Inorganic Chemistry, **University of Bath**

September 2005 promotion to **Senior Lecturer** in Bath

