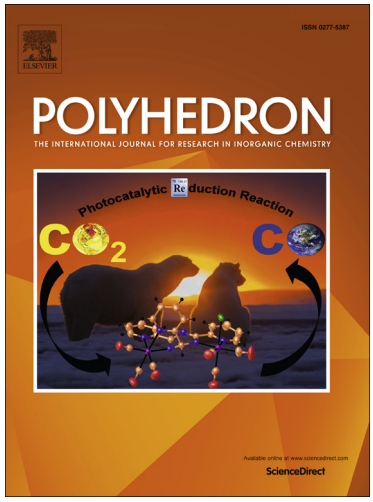

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PII: S0277-5387(14)00367-2
DOI: http://dx.doi.org/10.1016/j.poly.2014.05.050
Reference: POLY 10765

To appear in: *Polyhedron*

Received Date: 1 April 2014
Accepted Date: 8 May 2014

Please cite this article as: R.D. Köhn, A.G.N. Coxon, C.R. Hawkins, D. Smith, S. Mihan, K. Schuhen, M. Schiendorfer, G. Kociok-Köhn, Selective Trimerisation and Polymerisation of Ethylene: Halogenated Chromium Triazacyclohexane Complexes as Probes for an Internal 'Halogen Effect', *Polyhedron* (2014), doi: http://dx.doi.org/10.1016/j.poly.2014.05.050

Selective Trimerisation and Polymerisation of Ethylene: Halogenated Chromium Triazacyclohexane Complexes as Probes for an Internal 'Halogen Effect'

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Dedicated to Prof. John Bercaw on the occasion of his 70th birthday.

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ABSTRACT

A range of triazacyclohexane (R_3TAC) complexes of $CrCl_3$ with unsaturated N-substituents R have been prepared. The complexes with R = allyl (**3f**) and $CH_2CH(CH_2CH{=}CH_2)_2$ (**3h**) have been characterised by X-ray crystallography. Addition of HX or X_2 (X=Cl or Br) across the double bonds of the complexed ligand gives access to β- and γ-branched N-substituents containing three to twelve organic halogen atoms. The complexes with R = $CH_2CHBrCH_2Br$ (**3k**), $CH_2CH_2CX(^nC_5H_{11})_2$ (X=Cl (**3n**) and Br (**3o**)) have been characterised by X-ray crystallography. N-substituent chlorinated complexes can also be prepared via alkyl chloride containing amines as demonstrated for a crystal structure of a complex with R = $(CH_2)_3Cl$ (**3e**). Complexes with β-branched N-substituents give high selectivity for ethylene trimerisation to 1-hexene while complexes with γ-branched N-substituents are good ethylene polymerisation catalysts. The halogenated polymerisation catalysts give higher activities than their hydrogenated analogues, especially chlorine containing species. Chlorinated trimerisation catalysts demonstrated significantly improved 1-hexene selectivities, though activity was similar to hydrogenated alternatives. This lends support to the concept of a positive 'halogen effect' on the catalysis.

1. Introduction

The rapid expansion of oil and gas extraction from shale deposits in the USA and around the world has led to a significant increase in the availability of feed-stock gases [1]. Of significant commercial interest is therefore the conversion of light linear α-olefins, accessed via direct isolation, dehydrogenation or oligomerisation, into value-added products such as co-monomers, polymers and high performance fuels. Trimerisation and polymerisation are highly efficient synthetic routes to these higher molecular weight products and they are often based on chromium catalysts [2].

We have previously reported that triazacyclohexane complexes of $CrCl_3$ can be activated with MAO to produce effective ethylene polymerisation, [3] ethylene trimerisation [4] or α-olefin trimerisation [5] catalysts depending on the ligand design. Polyethylene produced by these species shows a similar branching and end group distribution to that of the Phillips catalyst [6]. $R_3TACCrCl_3$ catalysts can therefore be considered a good model for its investigation using a more defined system. This reactivity is attributed to the proposed ability of these species to form chromacyclic intermediates that