

# Triazacyclohexane complexes of chromium as highly active homogeneous model systems for the Phillips catalyst†‡§

Randolf D. Köhn,\*<sup>a</sup> Matthias Haufe,<sup>a</sup> Shahram Mihan\*<sup>b</sup> and Dieter Lilge<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Bath, Bath, UK BA2 7AY. E-mail: r.d.kohn@bath.ac.uk

<sup>b</sup> BASF AG, Kunststofflaboratorium, Abteilung Polyolefine ZKP/E-M 505, D-67056 Ludwigshafen, Germany. E-mail: shahram.mihan@basf-ag.de

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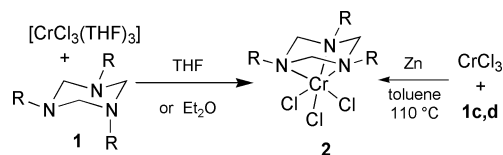
MAO activated 1,3,5-triazacyclohexane complexes of chromium(III) are highly active ethene polymerisation catalysts that resemble the Phillips catalyst in many important properties and may represent the first good homogeneous model system.

The heterogeneous Phillips catalysts<sup>1</sup> based on CrO<sub>3</sub>/SiO<sub>2</sub> for the polymerisation of ethene without co-catalysts produce a large fraction of the world production of HDPE (>7 M ton a<sup>-1</sup>).<sup>2</sup> The molecular weight of the polymer depends on the reaction temperature. When activated with metal alkyls the Phillips catalyst can also trimerise ethene to 1-hexene (as well as some dimers) which is *in-situ* co-polymerised giving a polymer with butyl side chains and other unusual end groups including additional methyl groups, vinylidene and some internal olefinic groups. In contrast to the Ziegler–Natta systems, the nature of the active species and the origin of the end groups is still a matter of debate. Many homogeneous model systems<sup>3</sup> show only limited activity<sup>4</sup> and most of them fail to reproduce the properties of the Phillips catalyst and a true model has yet to be found.

For several years we have been investigating the coordination chemistry of 1,3,5-triazacyclohexanes **1**.<sup>5</sup> The results suggest that it should be possible to generate cationic alkyl chromium complexes with low steric demand due to the small N–Cr–N angle which may be able to catalyse ethene polymerisation. Indeed, complex **2a** reacts with methylaluminoxane (MAO) to give a highly active catalyst. However, good solubility of the complexes is crucial to achieve high productivities. This solubility problem is solved by introducing longer alkyl chains as substituents in **2b–d** according to Scheme 1. The solubility increases dramatically and **2c** and especially **2d** become highly soluble in toluene. Complexes **2c** and **2d** can be prepared from CrCl<sub>3</sub> (stored under air), **1**, toluene and zinc powder by simple heating under a stream of argon.<sup>6</sup>

Since the ligands **1c,d** can also be prepared by heating the corresponding primary amine and paraformaldehyde in toluene a simple one-pot synthesis of **2** is possible.

The systems **2**/MAO have much higher activity than the best co-catalyst free complex **3**<sup>7</sup> and the best non-Cp system **4**/MAO<sup>8</sup> (Scheme 2). The activity is comparable to

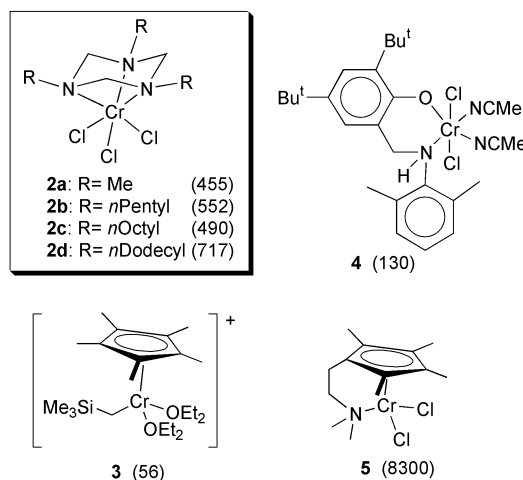


Scheme 1 Syntheses of the complexes **2**.

† Electronic supplementary information (ESI) available: synthetic, spectroscopic and analytical details of new compounds and the ethene polymerisation experiments. See <http://www.rsc.org/suppdata/cc/b0/b005842o/>

‡ Dedicated to Prof. H. Schumann on the occasion of his 65th birthday.

§ Chemistry of 1,3,5-triazacyclohexane complexes, Part 8. [Part 7, is ref. 5(a)].



Scheme 2 Chromium complexes in ethene polymerisation (comparison of activity in [kg (mol Cr)<sup>-1</sup> h<sup>-1</sup>]) (**2** at 40 °C and 1 bar ethene in toluene over 1 h).

[(nBuCp)<sub>2</sub>ZrCl<sub>2</sub>]/MAO under the same condition (650 kg (mol Cr)<sup>-1</sup> h<sup>-1</sup>) and the only more active chromium system is **5**/MAO from Jolly *et al.*<sup>4</sup>

Maximum activity is reached at MAO:Cr ≈ 300. Activation of **2** can also be achieved with 1.6 eq. DMAB (dimethylanilinium tetrakis(pentafluorophenyl)borate) and 20–50 eq. Al(iBu)<sub>3</sub>, giving similar activity (590 for **2a** and 390 for **2d**).

The molecular weights of the polymers under these conditions are around 40 000 (*M<sub>w</sub>*) with *M<sub>w</sub>*/*M<sub>n</sub>* = 2–4 which is typical for a single-site catalyst.

End group analysis of the polymers (IR, <sup>13</sup>C NMR) shows more methyl groups than expected and additional vinylidene and some internal olefin as well as the expected vinyl end groups in a distribution that is typical for end groups produced by the Phillips catalyst. Since the molecular weights of the polymers differ, the end groups are best compared relative to the total number of olefinic groups (set to 100%) (Table 1).

In addition, 1-hexene as the trimer of ethene and some decenes as ‘co-trimers’ of 1-hexene and ethene can be found in the solution, and butyl side chains in the polyethene are indicative of some 1-hexene built into the polymer. Thus, our system is also able to reproduce the selectivity for trimerisation.<sup>9</sup> Interestingly, analysis of the decene isomers by NMR

Table 1 Relative end group distribution with the sum of olefinic groups set to 100%

End group	CH <sub>2</sub> =CHR	CH <sub>2</sub> =CR <sub>2</sub>	RHC=CHR	Me
PE (Phillips) <sup>a</sup>	84–92%	7–13%	1–4%	150–300%
PE ( <b>2d</b> )	82%	12%	6%	240%
decenes ( <b>2d</b> )	87%	8%	5%	200%

<sup>a</sup> IR analyses of commercially available (BASF) Phillips HDPE products. Typical range under various conditions.

shows an end group distribution similar to the polymers (Table 1). Addition of 1-hexene to the solution increases the content of butyl side chains substantially and a co-polymer can be obtained. Similar to the Phillips catalyst, activated **2** gives molecular weights of polyethene that are highly dependent on the reaction temperature.

Thus, activated **2** represents the first true homogeneous model for the Phillips catalyst that can reproduce many important properties and the results indicate that the typical end group distribution may be closely linked to a required trimerisation activity. A comprehensive discussion of substituent effects and the link between trimerisation and polymerisation activity will follow in separate publications.

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