Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 689 (2004) 3641–3668

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Review

Advances in selective ethylene trimerisation – a critical overview

John T. Dixon, Mike J. Green, Fiona M. Hess, David H. Morgan *

Sasol Technology (Pty) Ltd, R&D Division, 1 Klasie Havenga Road, Sasolburg, 1947, South Africa

Received 7 April 2004; accepted 11 June 2004
Available online 28 July 2004

Abstract

Linear alpha olefins such as 1-hexene are widely used in the chemical industry. Over the past 15 years there has been considerable industrial interest in the selective trimerisation of ethylene to 1-hexene, which seems to be the preferred on-purpose route to this product. This article aims to provide a historical overview of all developments in the field of selective olefin trimerisation. During the discussion of the individual catalyst systems, special attention is also paid to features such as catalyst activity, reaction selectivity and relative catalyst cost, all of which would play a role in selecting the best technology. Various mechanistic aspects of this novel chemical reaction are also discussed in detail. The article concludes with a discussion on the major findings of a number of recent theoretical studies on trimerisation catalysis.

Keywords: Olefin; Ethylene; Trimerisation; Catalysis; 1-Hexene; Metallocycle

1. Introduction

Linear alpha olefins (LAOs) are useful intermediates for amongst others the manufacture of co-polymers, detergents, synthetic lubricants and plasticizer alcohols. Currently, LAO producers may broadly be grouped into two main categories, i.e. full range producers and on-purpose producers [1], depending on the chemistry of the processes.

The three largest full range producers of LAOs via ethylene oligomerisation are Shell, BP Amoco and Chevron Phillips [2]. An inherent feature of the chemistry of these metal catalysed ethylene oligomerisation processes is that they produce a mathematical distribution (Schulz–Flory or Poisson) of alpha olefins which very often does not match market demand. This product distribution provides a serious challenge to full range producers in that each alpha olefin market segment has different characteristics in terms of market size, growth, geography, fragmentation, technical services and logistics requirements. Although attempts have been made to skew the mathematical distribution of olefins to the higher value comonomer range (i.e. 1-C_6 and 1-C_8) [3], these modifications involve increased capital expenditure and operational complexity.

Currently, there are only a few on-purpose routes to LAOs due to the fundamentally different nature of the chemistry involved [1]:

- 1-Butene is made by ethylene dimerisation in the Middle East.
- Comonomer grade 1-hexene is made by ethylene trimerisation by Chevron Phillips. This plant was brought on line in 2003 as part of the Q-Chem I project in Qatar.
- 1-Hexene and 1-octene are extracted from Synthol streams at the Sasol facilities in Secunda, South Africa. Although this can be regarded as an on-purpose route

---

* Corresponding author. Tel.: +2716-960-5385; fax: +2711-522-1529.
E-mail address: Dave.Morgan@Sasol.com (D.H. Morgan).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.06.008

to specific LAOs, it is distinctly different from the above-mentioned processes since it is not based on selective ethylene oligomerisation.

Given the inherent problems facing the full range producers, the recent trend for R&D focus in this area is on novel on-purpose routes to alpha olefin comonomers. The approach which seems to be receiving the most attention at this stage, probably due to its high atom efficiency and superior economic performance, is selective ethylene oligomerisation, and in particular ethylene trimerisation. The activity from the industrial scientific community in terms of trimerisation patents seems to have reached a peak around 1996 (Fig. 1), whereas interest amongst the academic fraternity is clearly on the increase as is evidenced by the growing number of open literature publications (Fig. 2).

This paper will attempt to review the open and patent literature on selective olefin trimerisation and critically evaluate the various catalyst systems which have been developed. The main focus of this review will be on homogeneous chromium-based ethylene trimerisation systems; however, there are a few examples of trimerisation of higher olefins as well as non chromium-based systems which have been included. For the sake of completeness, a few heterogeneous trimerisation systems have also been included. As will be evident from the discussion, overall 1-hexene selectivities in excess of 99% are achievable with some of the trimerisation systems; hence the review will also cover the mechanistic aspects as well as molecular modelling studies on this remarkable olefin transformation.

In addition to these aspects, special attention will also be paid to catalyst activity, overall 1-hexene selectivity and relative catalyst cost, since these are key attributes for the commercialisation of processes based on these catalyst systems.

1.1. Ethylene trimerisation – the discovery

Although Chevron Phillips were the first to commercialise a process for the manufacture of 1-hexene via ethylene trimerisation, the key discoveries relating to this technology were in fact made by Manyik, Walker and Wilson of Union Carbide Corporation (UCC). Nearly 40 years ago these researchers filed a patent [4] on continuous processes for the production of PE. They observed that during the polymerisation of ethylene using Cr(III) 2-ethylhexanoate (Cr(III) 2-EH) activated by partially hydrolysed tri-isobutylaluminium (PIBAO), some of the ethylene trimerises to produce 1-hexene, which then co-polymerises with ethylene forming a polymer having butyl side chains.

Many years later Manyik et al. [5] published their discoveries concerning 1-hexene formation during the Cr(III) 2-EH/PIBAO catalysed polymerisation of ethylene. A detailed chromatographic analysis of the solvent from these polymerisation reactions revealed that 1-C_4, 1-C_6, 1-C_8 and 1-C_{10} were produced with 1-C_6 being predominant. The 1-C_6:1-C_4 was about 25:1 and in addition to 1-C_{10}, a number of branched decene isomers were also produced. The 1-C_6 content was, however, only about 1.1% of the liquid sample.

Marked differences in pressure and temperature dependence were observed on the rates of polymerisation and 1-hexene formation, the rate of 1-hexene formation being more sensitive to ethylene pressure than the rate of polymerisation. Furthermore, the rate of 1-hexene formation seemed to be dependent on the square of the ethylene pressure, implying a second order reaction in ethylene. Based on these results, the authors concluded that the 1-hexene was produced via a mechanism other than linear chain growth and they proposed a metallocycle mechanism to explain this second order dependence. Invoking this metallocycle mechanism, the authors

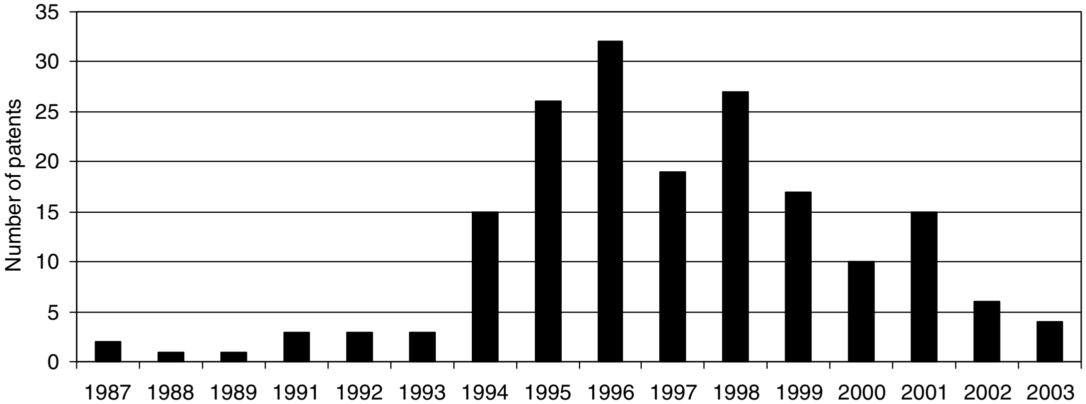


Fig. 1. Selective olefin trimerisation patents per year.

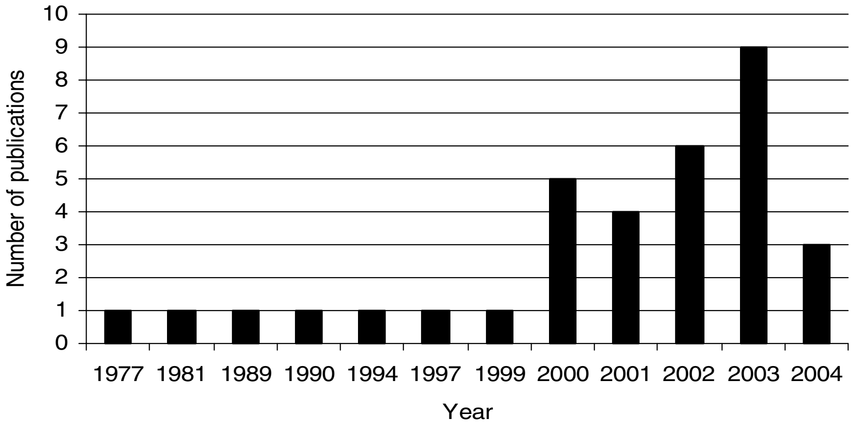


Fig. 2. Selective olefin trimerisation publications per year (up to March 04).

explained the formation of the branched decene isomers by the co-trimerisation of two ethylenes and a 1-hexene molecule.

A large number of additives were also evaluated as possible poisons or promoters of the catalyst system. Isoprene, piperyline and chloroprene as well as conjugated dienes such as 2-methoxybutadiene, cyclohexadiene and 3-ethylidenecyclohexene poisoned the reaction. Addition of 1,2-dimethoxyethane (DME), however, led to a marked increase in 1-hexene formation. This significant discovery formed the basis of the first truly selective ethylene trimerisation catalyst system which will be discussed in more detail later in the review.

2. Homogeneous trimerisation catalysts based on chromium

The discussion that follows summarises the development of homogeneous trimerisation catalysts based on chromium. Two major classes of ligands for chromium-based systems have been identified by the authors, i.e. anionic and neutral multidentate ligands. The bulk of the discussion will cover ethylene trimerisation systems although trimerisation of higher olefins such as 1-hexene and 1-dodecene is also included.

2.1. Chromium systems based on aromatic ligands

These ligands are mostly generated in the presence of a base which deprotonates a ligand precursor to form an anionic species for co-ordination to chromium. In many cases, the aromatisation of the system is the driving force for the formation of the anionic species. A common feature of these aromatic systems is that they are all activated by trialkyl aluminiums, which are for the most part, considerably less expensive than the corresponding alkyl aluminoxanes.

2.1.1. Pyrrolyl ligands – the development of the Phillips ethylene trimerisation catalyst

No review on selective olefin trimerisation chemistry would be complete without referring to the Phillips Petroleum catalyst system. This is simply because the Phillips system was the first example of a trimerisation catalyst that yielded 1-hexene in a greater than 90% overall selectivity (while concurrently producing less than 2 mass% PE) [6]. Chevron Phillips (a merger between Chevron and Phillips Petroleum Company) recently successfully commercialised this technology in Quatar 2003 [1]. Currently, this is still the only example of a commercial scale ethylene trimerisation plant.

In addition to this, more than 50% of the total number of olefin trimerisation patents filed to date (which greatly exceeds the total number of open literature publications, see Figs. 1 and 2) deal with the Phillips ethylene trimerisation catalyst system or variants thereof. A great number of these Phillips related patents are, however, process patents and not catalyst patents.

The discovery of the Phillips trimerisation catalyst systems occurred in the late 1980's when the catalytic properties of chromium pyrrolyl compounds were investigated. This study was initiated since chromium cyclopentadienyl complexes are used extensively as catalysts in the ethylene polymerisation industry and pyrrolide ligands are the closest heterocyclic analogues to cyclopentadienide ligands, both from electronic and steric perspectives [7]. Reagan [6,7] attempted to prepare a variety of chromium pyrrolyl complexes by treating $CrCl_2$ or $CrCl_3$ with various stoichiometric ratios of sodium pyrrolide in the presence of electron donor solvents such as tetrahydrofuran (THF).

Despite the fact that transition metal pyrrolyl compounds often exist as inorganic polymers, Reagan did manage to isolate and characterise a few such chromium pyrrolyl complexes. For example, he isolated a pentanuclear complex, $Cr_5(C_4H_4N)_{10}(C_4H_4O)_4$ from the reaction between $CrCl_2$ and two molar equivalents of sodium pyrrolide in THF. This complex, which is the minor reaction product, contained novel bridging amido-pyrrolyl ligands. The major reaction product was an inorganic polymer which is believed to contain the same type of bridging amido-pyrrolyl ligands based on the nearly identical infrared spectra of these two reaction products [7].

Surprisingly, the reaction between $CrCl_2$ and a molar excess of sodium pyrrolide in THF yielded two totally different compounds, namely the dianionic square planar complex $\{Cr(C_4H_4N)_4\}\{Na\}_2\cdot(C_4H_4O)_2$ as the major product, and the octahedral complex $\{Cr(C_4H_4N)_5\cdot(C_4H_4O)\}\{Na\}_2\cdot(C_4H_4O)_4$ as the minor product. The formation of the Cr(III) octahedral complex was attributed to the presence of 5–10 weight% $CrCl_3$ in the commercial sample of $CrCl_2$ used for the preparation [6].

Finally, the reaction between $CrCl_3$ and three molar equivalents of sodium pyrrolide in THF yielded exclusively an inorganic polymer. The x-ray fluorescence data of this reaction product indicated that it consisted of multiple $Cr(C_4H_4N)_2Cl$ units [7].

Although the preparation of the above chromium pyrrolyl compounds might not be regarded by some as ground-breaking, the discovery of their catalytic properties certainly was. All the above complexes (except the octahedral Cr(III) complex $\{Cr(C_4H_4N)_5\cdot(C_4H_4O)\}\{Na\}_2\cdot(C_4H_4O)_4$ which apparently was not evaluated) were found to be catalytically active towards ethylene oligomerisation at 90 °C and 38 bar pressure upon activation with approximately 25 molar equivalents of triethylaluminium (TEA).

These complexes were also found to be catalytically active when supported on $AlPO_4$, SiO_2 and Al_2O_3. The reaction selectivity and activity seemed to be a function of the choice of the starting chromium pyrrolyl complex, whether supported or not and the type of support used during catalyst preparation. Although a catalyst activity exceeding 10,500 g/g Cr per hour was achieved using the Al_2O_3-supported pentanuclear complex $Cr_5(C_4H_4N)_{10}(C_4H_4O)_4$, this reaction yielded only 31% liquid oligomers apart from the 69% PE produced [7]. It was, however, possible to achieve selectivities in excess of 99% towards liquid oligomers when using the Cr(III) polymer consisting of $Cr(C_4H_4N)_2Cl$ units. On the other hand, this reaction exhibited a considerably lower catalyst activity of only 1030 g/g Cr per hour. The most striking aspect of these liquid oligomer products was that they contained up to 90.5% hexenes of which approximately 92% was 1-hexene. It was thus possible at this stage to obtain overall selectivities towards 1-hexene in excess of 83%, while producing less than 2% PE [6].

During the next few years, Phillips Petroleum Company made considerable improvements to their original discovery, both from catalyst development and process development perspectives. For example, Reagan and his co-workers [8] discovered that it was possible to prepare an active catalyst without using defined chromium pyrrolyl complexes as catalyst precursors. In fact, one could obtain an active trimerisation catalyst by simply combining a chromium (III) alkanoanate, such as Cr(III) 2-EH, with pyrrole and TEA in a paraffinic solvent, such as cyclohexane, shortly before conducting the oligomerisation reaction. The presence of an aromatic hydrocarbon solvent, such as toluene, during catalyst preparation led to improved catalyst stability so that the catalyst system could even be successfully recycled three to four times [9]. However, the presence of an excess quantity of an aromatic hydrocarbon solvent in the reaction mixture (after catalyst preparation) had a detrimental effect on the catalyst activity [8]. Higher catalyst activities could also be achieved when there was little or no stirring present when the co-catalyst (TEA) is added during catalyst preparation to a solution containing the chromium precursor and the ligand [10].

2,5-Dimethylpyrrole (DMP) seemed to be Phillip's preferred ligand due to its excellent performance during catalysis. This pyrrole derivative is also preferred from a practical point of view due to its higher air, light and temperature stability. In addition to this, Phillips also discovered that the presence of a halogen compound, such as diethyl aluminium chloride (DEAC), 1-bromobutane, $GeCl_4$ and $SnCl_4$, during the catalyst preparation led to marked improvements in both the catalyst activity and selectivity towards 1-hexene formation [8].

Finally, Phillips extended the scope of their trimerisation technology to tandem trimerisation co-polymerisation where co-polymers with densities ranging from 0.913 to 0.948 g/ml were prepared in a single reactor using a mixture of the Phillips trimerisation catalyst (on an aluminophosphate support) and well-known supported chromium- and titanium-based polymerisation catalysts [11].

By 1999 Phillips had improved the performance of their ethylene trimerisation catalyst to such an extent that they achieved catalyst activities exceeding 94,000 g/g Cr in 36 min (156,666 g/g Cr per hour) at a reaction temperature of 115 °C and a reaction pressure of 100 bar. This catalyst was prepared by combining Cr(III) 2-EH, 2,5-dimethylpyrrole, diethylaluminium chloride and TEA in toluene in molar ratios of 1:3.3:7.8:10.8 at room temperature using a nitrogen purge to stir the reagents. The trimerisation reaction yielded 99.85% liquid oligomers containing 93.83% hexenes of which 99.2% was 1-hexene (93% overall 1-hexene). The main side products were a mixture of linear and branched decenes (5.38%) [10].

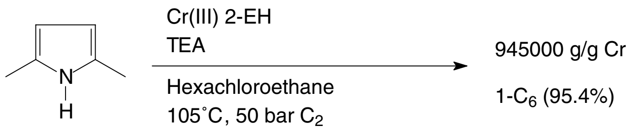
Shortly after the discovery of the Phillips trimerisation catalyst, a number of other commercial companies started to file patents relating to this catalyst system. The most prolific of these companies was Mitsubishi Chemical Corporation. They, for example, discovered that catalysts prepared with non co-ordinating Lewis acids, such as $B(C_6F_5)_3$, in addition to Cr(III) 2-EH, pyrrole and TEA exhibited significantly higher activities than catalysts prepared without it [12]. Mitsubishi also developed a protocol whereby they prepared the Phillips catalyst in situ during a continuous trimerisation reaction [13]. By employing this in situ protocol (using chromium(III) 2-ethylhexanoate, 2,5-dimethylpyrrole, hexachloroethane and triethylaluminium in molar ratios of 1:6:4:40) and by carefully controlling the molar ratio of 1-hexene to ethylene inside the reactor (at less than 0.5:1), they managed to obtain unprecedented catalyst activities of up to 945,000 g/g Cr in 15 min (3,780,000 g/g Cr per hour) at 105 °C and 50 bar (see Scheme 1) [13]. The reaction mixture contained 99.96% liquid oligomers including 95.9% hexenes of which 99.5% was 1-hexene (95.4% overall 1-hexene).

Other companies that have filed patents or published open literature articles on variants of the Phillips catalyst system include Sumitomo Chemical Company [14], BASF [15], Idemitsu Kosan Company [16], Chinese Petroleum Group [17], Sasol Technology [18] and Beijing Yanshan Petrochemical Company [19]. In most of these cases, new variants of one of the three essential catalyst components were used to prepare the active trimerisation catalyst. Variants used include the use of diisobutylaluminium 2,5-dimethylpyrrolide [14], 2-(5′-bromopentyl) pyrrole [18], (hexahydro-1,3,5-trioctyl-1,3,5-triazine)$CrCl_3$ [15] and partially hydrolysed triethylaluminium [16]. The catalytic performance of most of these catalyst variations are, however, fairly moderate compared to the optimised results obtained by Phillips and Mitsubishi with the 'classic' Phillips catalyst system.

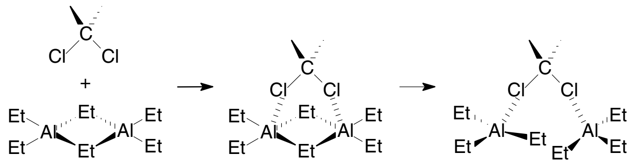
Despite the prominence of the Phillips trimerisation catalyst system, there is little public knowledge concerning the fundamental aspects of this catalyst and to date there are only two non-theoretical open literature articles relating to this topic. In the first of these, Yang et al. [20] investigated the role of the organo-chloro compounds in this system by conducting a large number of catalytic runs using different chloro compounds during catalyst preparation as well as different molar ratios of each of the catalyst components. They observed that the catalytic activity and selectivity of this reaction were strongly affected by variations in both of these. In general, there seemed to be a direct correlation between the number of chloro atoms in the organo-chloro catalyst component and both the 1-hexene selectivity and ethylene conversion rate. This pattern of catalyst behavioural changes has been found to be qualitatively more consistent with the number of geminal chloro atoms on the specific organo-chloro compound rather than with the total number of chloro atoms. The authors proposed that this observation can be attributed to the breaking up of the dimeric form of TEA by the geminal chloro compound (which acts as a Lewis base) to yield monomeric TEA (see Scheme 2). It is believed that the monomeric TEA is advantageous to the formation of the active chromium species due to its better Lewis acid properties.

The second of these open literature publications focuses on the coating of the activated Phillips trimerisation catalyst system with paraffin waxes. It was shown by Hu and co-workers [21] that the coating of this catalyst system with paraffin wax led to a large improvement in its stability towards air exposure. For example, coated catalyst that was exposed to air for 24 h at room temperature, retained 88% of it original activity while yielding 1-hexene in the same overall selectivity of 92.7%. The authors also investigated the oxidation state of the activated catalyst using X-ray photoelectron spectroscopy which indicated that approximately 93–95% of the chromium existed as Cr^{3+}, with the remainder being Cr^{6+}. The authors thus ascribed the Cr^{3+} state to the 1-hexene yielding catalyst species.

The final aspect relating to the Phillips trimerisation catalyst system to be dealt with, relates to the use of ionic liquids as solvents for this catalyst. Sasol Technology [22] discovered that imidazolium-based ionic liquids containing $[Et_{3n}Al_nCl]$-based anions could successfully be used as solvents for the Phillips trimerisation catalyst. Ionic liquids usually separate quite readily from organic compounds, such as 1-hexene, to yield a biphasic mixture. Easy separation from the trimerisation reaction products would therefore facilitate the recycling/re-use of the Phillips catalyst. By using [1-ethyl-2,3,-dimethylimidazolium] $[Et_{3n}Al_nCl]$ as the solvent, ethylene trimerisation reactions at 115 °C and 50 bar yielded 75% hexenes containing 87% 1-hexene (65.3% 1-C_6 overall) in catalyst activities exceeding 25,000 g/g Cr per hour over a period of 30 min. The catalyst was prepared using Cr(III) 2-EH, 2,5-dimethylpyrrole and TEA in molar ratios of 1:10:20. This study was also subsequently extended to higher olefin substrates such as 1-pentene and 1-decene [22,23]. Ranwell and Tshamano [23]



Scheme 1.



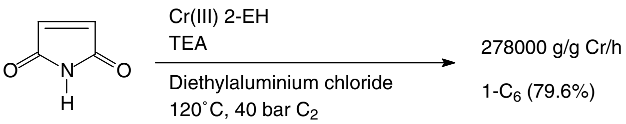
Scheme 2.

discovered that although only very low conversions of 1-decene to oligomers (consisting of 67% C30 trimers) could be achieved using the Phillips catalyst system in organic solvents/reagents, both the rate of conversion and the reaction selectivity increased considerably when these reactions were conducted in ionic liquids. Thus, combining Cr(III) 2-EH, 2,5-dimethylpyrrole, TEA and 1-decene in molar ratios of 1:7:20:200 in [1-butyl-3-methylimidazolium] [$Et_{3n}Al_nCl$] resulted in a 46% conversion of the 1-decene to 91% C30 trimers at 25 °C in 24 h. The viscosity index of the C30 fraction of this reaction mixture is also favourably high at 130, which suggests that this cut could be a superior poly alpha olefin (PAO) product.

2.1.2. Maleimidyl ligands

Maleimide is in many respects very similar to pyrrole, especially from electronic and molecular orbital perspectives. In view of the Phillips trimerisation catalyst, a trimerisation catalyst based on maleimide should be quite feasible. Tosoh Corporation did indeed develop such a catalyst system during the latter part of the 1990s [24]. As with the Phillips catalyst the Tosoh system is based on three components, namely a chromium precursor (typically Cr(III) 2-EH), maleimide and an alkylaluminium compound [24]. Tosoh Corporation in essence used the same approach as Phillips and others to optimise their catalyst system. For example, they discovered that halogen containing compounds, such as Et_2AlCl and $GeCl_4$, had a similar positive effect on both the catalyst activity and reaction selectivity as was found for the Phillips catalyst [25]. Thus, by using Cr(III) 2-EH, maleimide, TEA, diethylaluminium chloride in molar ratios of 1:60:430:160 they managed to obtain considerable catalyst activities of up to 278,000 g/g Cr per hour at 120 °C and 40 bar (see Scheme 3). The reaction mixture contained 98.5% liquid oligomers including 86.7% hexenes of which 93.2% was 1-hexene giving 79.6% overall 1-hexene.

Tosoh also investigated the influence of a number of other compounds on the catalyst performance. These include O-, S- and P-containing compounds (e.g. dimethoxyethane) [25], non-conjugated dienes (e.g. 1,5-cyclooctadiene) [26] and aromatic solvents (e.g. toluene) [27]. Most of these so-called ‘promoters’ had a marginal or even detrimental influence on the catalyst performance. Tosoh Corporation also investigated the use of different maleimidyl containing precursors such as the reaction product between triisobutylaluminium or diisobutylaluminium hydride and maleimide during catalyst preparation (a similar approach was employed with pyrrolyl ligands by Sumitomo Chemical Corporation [13]), but without a marked improvement in the catalyst performance [28]. Finally they also proved that the catalyst could be successfully supported on SiO_2, although it also tended to produce significant quantities of PE (typically 20%) in these reactions [29].



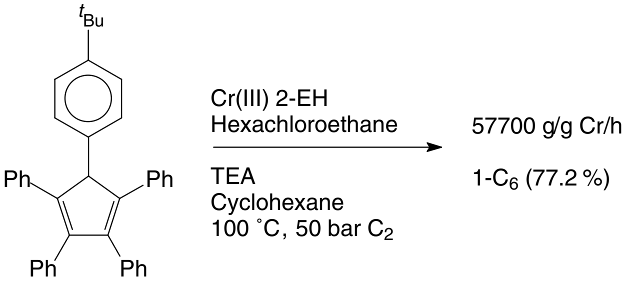
Scheme 3.

Although this catalyst system is definitely a noteworthy equivalent to the Phillips trimerisation catalyst, the overall selectivity towards 1-hexene generally seems to be 12–15% lower which definitely would make this system less desirable from an economic perspective.

2.1.3. Cyclopentadienyl ligands

As indicated in Section 2.1.1, cyclopentadienyl (Cp) ligands and pyrrolyl ligands are very similar, both from electronic and steric perspectives [7]. By analogy, they should also be good ligands for chromium catalysed olefin trimerisation. However, up until recently, chromium-based cyclopentadienyl complexes have only been shown to be active polymerisation catalysts [30,31]. It is worth mentioning that Jolly et al. [32] used cyclopentadienyl chromium metallocycle model complexes to suggest the potential existence of the metallocyclopentane and -cycloheptane intermediates for the trimerisation mechanism. However, these cyclopentadienyl chromium metallocycle complexes were found to be very active ethylene polymerisation catalysts, giving activities of 307,715 g PE/g Cr per hour. On the contrary, it was shown by Sasol Technology that when bulky aromatic substituents are introduced onto the cyclopentadienyl ring, highly active trimerisation catalysts can be obtained [33,34].

The best results in terms of overall 1-C_6 selectivity were achieved at a reaction temperature of 100 °C and an ethylene pressure of 50 bar with 5-(4-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopentadienyl as ligand using a catalyst prepared with Cr(III) 2-EH:ligand:hexachloroethane:TEA in molar ratios of 1:3:2.5:45 (see Scheme 4). This gave a reaction mixture containing 99.5% liquid products comprising 0.5% C_4, 93.5% C_6 (83% 1-C_6,



Scheme 4.

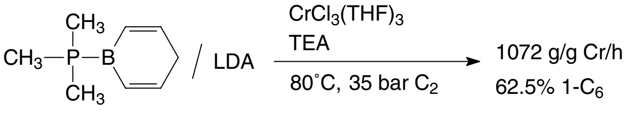
77.2% 1-C_6 overall), and 6% C_{10}+. The catalyst activity was 57,700 g/g Cr per hour.

A substantial amount of internal hexenes were also formed during these catalytic runs. It was also found that the α-selectivity within the hexenes was highly dependent on the substituents of the cyclopentadiene ring. For example, the use of 1,2,3,4-tetraphenyl-cyclopentadienyl as ligand yielded only 61.7% 1-hexene whereas using 5-(4′-*t*-butylphenyl)-1,2,3,4-tetraphenyl-cyclopentadienyl yielded 83% 1-hexene. The reaction temperature also seemed to influence selectivity/activity, with lower temperatures promoting higher activity and 1-hexene selectivity within the C_6 fraction, but also promoting more PE and lower C_6 selectivity. For example, conducting a reaction using the same molar ratios as in the above example, but at 70 °C, produced an overall 1-C_6 selectivity of 73.4% with a catalyst activity of 93,500 g/g Cr per hour.

In addition to the high cost of substituted Cp ligands, the major Achilles heel of this catalyst system from an economic viability viewpoint is the low 1-C_6 selectivity within C_6 fraction (17% internal hexenes). The process economics would be negatively influenced by the difficult separation of 1-C_6 from other C_6 isomers.

2.1.4. Boratabenzenyl ligands

Boratabenzenyl and cyclopentadienyl anions are often considered to be isoelectronic [35] and by analogy to the systems discussed in Sections 2.1.2 and 2.1.3, one would also expect the existence of a trimerisastion catalyst system based on these ligands. Mitsubishi Chemical Industries did indeed investigate these ligands and found them to promote 1-hexene formation, although at very moderate catalyst activities [36]. Thus, trimethylphosphinoboracyclohexadiene in tetrahydrofuran (THF) was treated at −78 °C with lithium diisoproplyaminde (LDA). The product of this reaction was added to 0.7 molar equivalents of $CrCl_3(THF)_3$ in THF solvent to yield an uncharacterised chromium boratabenzenyl compound in 6 h at room temperature. Activation of this compound with TEA and conducting the ethylene oligomerisation reaction at 80 °C and 35 bar ethylene pressure yielded a catalyst activity of 1072 g/g Cr per hour (see Scheme 5). The reaction mixture contained >99.9% liquid oligomers including 85.8% hexenes of which 75.1% was 1-hexene, giving an overall selectivity to 1-hexene of 62.5%.



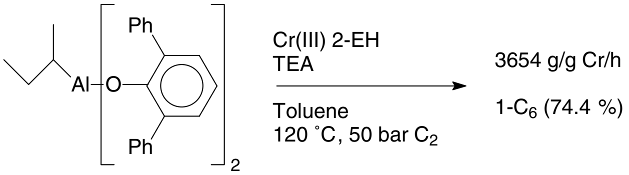
Scheme 5.

2.1.5. Aryloxide ligands

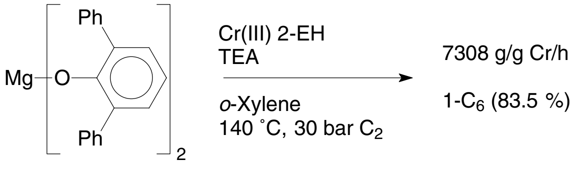
The first application of this class of ligands in selective ethylene oligomerisation was by the Institut Francais du Petrole (IFP) [37]. They filed a patent on an ethylene trimerisation catalyst system comprising a chromium source, an aryloxyaluminium compound of general formula $R_nAl(R'O)_{3-n}$ and a trialkylaluminium activator. According to this patent, the best ethylene trimerisation results were achieved using a system comprising Cr(III) 2-EH, bis(2,6-diphenylphenoxy)isobutylaluminium and TEA at molar ratios of 1:8:8. When the reaction was carried out in toluene at 120 °C and 50 bar ethylene pressure, it afforded 0.4% C_4, 74.5% C_6 (99.8% 1-C_6, 77.4% 1-C_6 overall), 0.9% C_8, 6.2% C_{10+} and 18% PE (see Scheme 6). The reaction consumed 19 g of ethylene in 60 min, giving a catalyst activity of 3654 g/g Cr per hour.

Two years later IFP filed a catalyst patent [38] on a related system comprising a chromium source, an aryloxy component of general formula $M(RO)_{2-n}X_n$ wherein M is magnesium, calcium, strontium or barium and X is a halogen. In the best example, Cr(III) 2-EH, bis(2,6-diphenylphenoxy)magnesium and TEA at molar ratios of 1:1:3 in *o*-xylene at 140 °C and 30 bar ethylene pressure afforded a reaction mixture comprising 1.3% C_4, 84.4 % C_6 (98.9% 1-C_6, 83.5% 1-C_6 overall), 1% C_8, 2.3% C_{10+} and 11% PE (see Scheme 7). The reaction consumed 19 g of ethylene in 30 min giving an activity of 7308 g/g Cr per hour, making this system twice as active as the previous system based on aryloxyaluminium compounds.

Sasol Technology has also investigated the use of aryloxide ligands for Cr-based ethylene trimerisation and have patented [39] and published [40] results showing improvements when the reaction is carried out in an aromatic ether solvent such as anisole. Surprisingly this improved both the selectivity and activity of the catalyst system when compared to reactions carried out in xylene



Scheme 6.



Scheme 7.

as solvent. In addition to this the authors demonstrated that a preformed aryloxyaluminium complex was not necessary for catalytic activity and that the catalysis could be carried out by mixing the components in situ.

Catalytic runs as well as spectroscopic evidence suggested that the anisole acts as both solvent and catalyst component. In a typical run using Cr(III) 2-EH, 2,6-diphenylphenol and TEA at molar ratios of 1:14.5:20, the catalysis in anisole produced 86.4% liquid oligomeric products of which 89.7% was C_6 (see Scheme 8). The 1-hexene selectivity in the C_6 fraction was 98.9% and overall selectivity to 1-C_6 was 77.5%. 13.6% PE was produced and the catalyst activity was around 23,000 g/g Cr per hour.

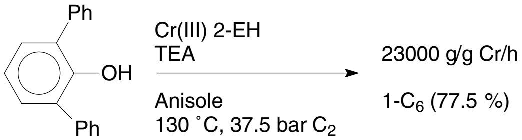
Selective trimerisation, albeit at very low activities, was also observed when the reaction was carried out in anisole in the absence of any 2,6-diphenylphenol. In addition to a number of different 2,6-disubstituted phenols, the authors also investigated the use of enolates as well as 2,6-disubstituted thiophenols as ligands, with limited success.

Finally, this catalyst system in anisole as reaction solvent was found to be very sensitive to temperature effects, giving mainly PE at 100 °C, and mainly linear chain growth products at temperatures exceeding 130 °C.

In summary, although aryloxide ligands are relatively inexpensive, it appears that ethylene trimerisation catalysts based on Cr(III) and aryloxide ligands are only capable of modest catalyst activities (<30,000 g/g Cr per hour) and 1-C_6 selectivities (ca. 83% overall). As opposed to the Cp system described earlier, 1-C_6 selectivities within the C_6 fraction are very high (>98%). From a commercialisation point of view however, the major stumbling block is the high PE content (>9%) of reaction mixtures, which would complicate the design of a process based on this catalyst.

2.2. Chromium systems based on multidentate heteroatomic ligands

A common feature of multidentate heteroatomic ligands is that they contain donor sets which form co-ordinate bonds with chromium. Most of the ligand systems described in this section are either bidentate or tridentate. The tridentate systems can further be subdivided into systems where the procatalyst has a meridional arrangement of the ligand and those which have a facial arrangement of the ligand. Those having a meridional arrangement have donor sets in which the outer donor atoms are soft donors allowing for facile association–dissociation equilibria and in general these systems provide extremely selective ethylene trimerisation catalysts. A further feature of these multidentate systems is that many are activated by alkyl aluminoxanes, which due to their high cost, necessitate catalyst systems which are extremely active and selective for an economically feasible technology.



Scheme 8.

2.2.1. Ligands based on oxygen donors

Surprisingly, more than a decade elapsed after Manyik's discovery that ethylene could be trimerised to 1-hexene before the first truly selective ethylene trimerisation system was patented. Manyik et al. had provided the clue that donor ligands such as dimethoxyethane promoted the reaction and picking up on this, Briggs [41] of the Long Range Catalyst Group of UCC patented an ethylene trimerisation catalyst system comprising a chromium compound, a hydrolysed hydrocarbylaluminium compound and a donor ligand. This donor ligand was selected from hydrocarbyl isonitriles such as *t*-butyl isonitrile, amines such as tetramethylethylene diamine and ethers of the general type $CH_3O(CH_2CH_2O)_nCH_3$. The best ethylene trimerisation activities and selectivities were obtained using DME as donor ligand.

Briggs later published more details concerning the development of this ethylene trimerisation catalyst [42]. In the best catalysis example, Cr(III) 2-EH, PIBAO and DME at a molar ratio of 1:2:10 in heptane solvent at 95 °C and 28–35 bar ethylene pressure gave 74% overall 1-hexene selectivity and a catalyst activity (TOF) of 1.2 $Cr^{-1}s^{-1}$ (2086 g/g Cr per hour). The remainder of the product was PE, an analysis of which revealed no 1-hexene incorporation. In addition to 1-hexene and PE, small amounts of C_4 and C_8 were also produced.

Although the mechanistic aspects will be discussed in more detail in a later section of the review, it is noteworthy that Briggs was the first to implicate both metallocyclopentane and metallocycloheptane intermediates in this selective production of 1-hexene.

Further work on the system by Levine and Karol [43] of UCC revealed that the presence of CO_2 could increase the efficiency of the Cr(III)/DME trimerisation catalyst toward 1-C_6 formation.

Following on from UCC's discoveries concerning DME as donor ligand, Idemitsu Chemical Company filed two related patents in the mid 1990s. The catalyst systems were in essence the same as UCC's except that aluminium alkoxides were used as activators. In one example [44], a solution of Cr(III) 2-EH and aluminium *t*-butoxide in cyclohexane was reacted with 3.14 g ethylene at 100 °C and 34 bar for 23 min to give 2.64 g product containing 84% 1-C_6, 3% 1-C_8, 2% C_{10+} and 11% PE. The catalyst activity was 5298 g/g Cr per hour.

In the second patent [45] ethylene was oligomerised in the presence of a catalyst obtained by mixing Cr tris(adamantanecarboxylate), DME, aluminium *t*-butoxide and triisobutylaluminium at molar ratios of 1:100:1000:50 at 100 °C and 34 bar ethylene pressure for 50 min to give 82% 1-C_6, 10% 1-C_8 and 8% PE. The catalyst activity was 6970 g/g Cr per hour.

It is clear from the above discussion that these chromium systems based on ether ligands are not sufficiently active or selective to be considered for commercial application. On the other hand, however, the fact that DME appears to improve the selectivity to 1-hexene suggests that it may be considered as a selectivity improving additive for other catalyst systems.

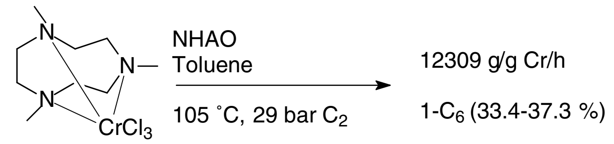
2.2.2. Ligands based on nitrogen donors

Triazacycloalkane ligands. Wu [46] has suggested that the preferred nitrogen-based ligands for oligomerisation are sterically demanding ligands such 1,4,7-trimethyl-1,4,7-triazacyclononane which co-ordinate facially to the chromium. He reasoned that these ligands would permit both ethylene trimerisation and oligomerisation, while at the same time inhibit polymerisation. In a patent to Albemarle Corporation [46], Wu describes a process for the selective oligomerisation of ethylene in the presence of a catalyst system comprising Cr complexes of triazacyclononane using aluminoxanes as activators. This process provides a Schulz–Flory distribution of alpha olefins which is selectively enriched in 1-hexene, without the concurrent formation of excessive amounts of vinylidine olefins and PE.

In line with his reasoning concerning the necessity of steric bulk for oligomerisation over polymerisation, he found that in the absence of substitution on the nitrogens, the catalyst system only gave polymerisation. For any given catalyst system, lower reaction temperatures (ca. 30 °C) also favoured polymerisation over oligomerisation. Interestingly, the catalyst lifetime was prolonged by the combination of catalyst components in situ under ethylene pressure. Similar observations have also been made for the Phillips catalyst system [10,13].

In one example, ethylene was oligomerised at 105 °C and 29 bar in the presence of [1,4,7-trimethyl-1,4,7-triazacyclononane]$CrCl_3$ and *n*-hexylaluminoxane (NHAO) at a molar ratio of 1:80 in toluene to give a product containing 9.4% C_4, 39.3% C_6, 10% C_8, 8.5% C_{10}, 6.9% C_{12}, 6% C_{14}, 5% C_{16}, 4% C_{18} and 10.9% C_{20+}. The selectivity for linear alpha olefins was 85–95% and 32 g of ethylene was consumed over 30 min giving an activity of around 12,309 g/g Cr per hour (see Scheme 9). The major product impurities were internal olefins, cyclic olefins and paraffins.

Using the Schulz–Flory equation, the expected amount of C_6 was calculated to be around 10%, clearly showing that both the metallocycle (see Section 6.1) as well as the linear chain growth mechanism were in operation with this catalyst system.



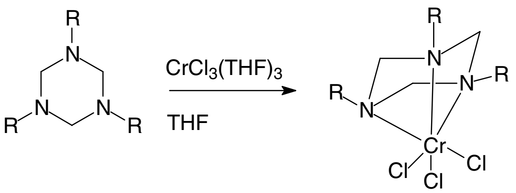
Scheme 9.

Köhn and Kociok-Köhn [47] have subsequently demonstrated the facile synthesis of the related and highly stable *N*-alkyl triazocyclohexane complexes of Cr(III) and Fe(III). Crystal structure determinations revealed that these ligands are η^3 co-ordinated to the metal (see Scheme 10).

In searching for homogeneous analogues for the CrO_3/SiO_2 polymerisation catalyst (Phillips), Köhn et al. [48] went on to demonstrate that these 1,3,5-triazacyclohexane chromium complexes could be activated by methylaluminoxane (MAO) or $[PhMe_2NH][B(C_6F_5)_4]$/*i*-Bu_3Al to form active ethylene polymerisation catalysts. The *N*,*N*,*N*-trimethyl analogue when activated by MAO, gave polymerisation catalysts giving a moderate activity of 455 kg/mol Cr per hour (8751 g/g Cr per hour). However, when the highly soluble *N*,*N*,*N*-tridodecyl analogue was tested at 40 °C and 1 bar ethylene it gave an activity of 717 kg/mol Cr per hour (13,780 g/g Cr per hour). Analogous to observations with the heterogeneous CrO_3/SiO_2 polymerisation catalyst of Phillips, 1-hexene and decenes as 'co-trimers' of 1-hexene and ethylene could be found in solutions of these polymerisation reactions. In addition to this, ^{13}C NMR analysis revealed the presence of butyl side chains in the PE, indicative of 1-hexene incorporation during polymerisation. These findings led the authors to postulate that this was the first truly homogeneous model for the Phillips CrO_3/SiO_2 polymerisation catalyst [49].

Köhn et al. [50] subsequently showed that these triazacyclohexane complexes of Cr(III) were capable of trimerising higher alpha olefins such as propene, 1-hexene and styrene. Up until this time no other trimerisation catalysts were shown to be capable of this transformation with higher olefin substrates.

At room temperature, the trimerisation of 1-hexene ceased after a few hours at about 80% conversion. However, up to 90% alpha olefin conversion could be



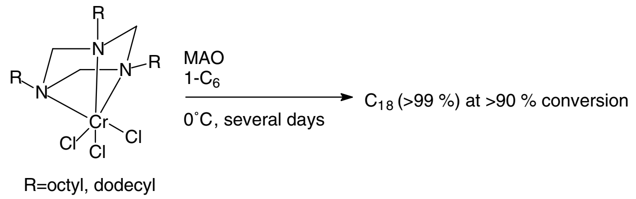
Scheme 10.

achieved if the reaction mixture was refrigerated for several days (see Scheme 11). The selectivity of the catalyst system toward trimer formation was excellent and dimers and tetramers could only be found in less than 1%. Donor functionalised olefins and donor solvents tended to deactivate the system and internal olefins and conjugated dienes could not be trimerised. The analogous methyl-substituted triazacyclononane systems were shown to be incapable of trimerising higher alpha olefins under the same reaction conditions and the authors alluded to the importance of low steric demand of complexes for reactivity toward higher alpha olefins.

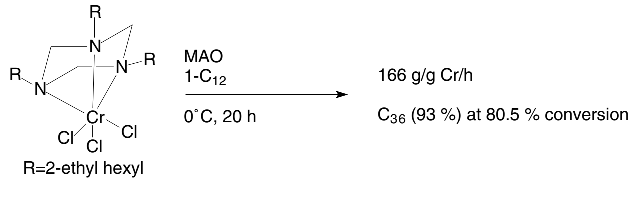
Wasserscheid et al. [51] have used triazacyclohexane complexes of Cr(III), activated by MAO, for the selective trimerisation of 1-decene and 1-dodecene. After hydrogenation, the C30 and C36 oligomeric products displayed the required viscosity indices as well as low pour points and low vapour pressures, making them attractive candidates for use as synthetic lubricants. High trimer selectivities make this trimerisation catalyst superior to the well known BF_3-ROH catalysts for 1-decene oligomerisation.

A number of 1-dodecene trimerisations were carried out using 100 equivalents of MAO in toluene as reaction solvent at 0 °C over 20 h run times (see Scheme 12). The *N*,*N*,*N*-tri-2-ethylhexyl analogue gave an olefin conversion of 80.5% yielding 93% C_{36}, 7% internal C_{12}'s and a catalyst activity of 1026 mol 1-C_{12} converted/mol Cr (166 g/g Cr per hour).

The R groups on the nitrogen were shown to affect the catalyst activity and trimerisation/isomerisation ratio. A higher degree of branching of the R group in the alpha position enhanced the undesired isomerisation reaction and dramatically reduced the catalyst activity. The *N*,*N*,*N*-tridodecyl analogue gave very high 1-dodecene conversion (97.7%), but the trimer selectivity was only 81% with 19% internal C_{12} being produced. Kinetic investigations with 1-dodecene revealed an induction period, followed by a characteristic catalyst deactivation profile with time.



Scheme 11.



Scheme 12.

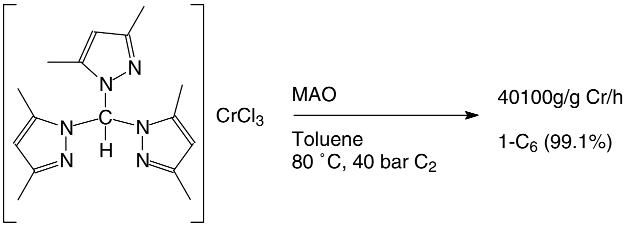
The catalytic reaction was shown to follow the classical metallocycle mechanism (see Section 6.1), producing either internal olefins or vinylidines (no alpha olefins were observed in the trimer product). After hydrogenation, 4 main trimer products were formed, consistent with the product distribution expected from a metallocycle mechanism.

Tris(pyrazolyl)methane ligands. Tris(pyrazolyl)methane ligands have been extensively reviewed as complexes of copper(I), silver(I), cadmium(II), lead(II) and thallium(II) [52]. Tosoh Corporation, however, made the discovery that chromium complexes of tris(pyrazolyl)methane ligands, when activated by MAO or trialkyl aluminiums, gave active and selective ethylene trimerisation catalysts. In one such patent [53], four complexes, i.e. tris(3,5-dimethyl-1-pyrazolyl)methanechromium trichloride, tris(3-phenyl-5-methyl-1-pyrazolyl)methanechromium trichloride, tris(3-phenyl-1-pyrazolyl)methanechromium trichloride and tris(3-(4-tolyl)-1-pyrazolyl)methanechromium trichloride were synthesised. Upon activation with MAO or mixtures of MAO and *n*-octyl$_3$Al or *i*-Bu$_3$Al, the complexes gave active and selective ethylene trimerisation catalysts. These complexes were prepared by reacting the respective tris(pyrazolyl)methane ligands with $CrCl_3(THF)_3$ in THF as solvent and, as with the triazacycloalkane systems discussed previously, were found to co-ordinate facially to the chromium.

The best result was achieved using tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride activated by 360 molar equivalents of MAO at 80 °C and 40 bar ethylene pressure (see Scheme 13). This afforded a reaction mixture containing 0.1% C_4, 99.6% C_6 (99.5% 1-C_6, 99.1% 1-C_6 overall) and 0.3% C_{8+}. The activity of the catalyst was 40,100 g/g Cr per hour.

This system provides rather impressive overall 1-hexene selectivities and good catalyst activities. In contrast to many other nitrogen-based ligand systems, tris(pyrazoly)methane ligands are stable and easy to handle.

Tosoh filed a number of related patents on this system, reporting catalyst activities as low as 3 g/g Cr per hour [54–57].



Scheme 13.

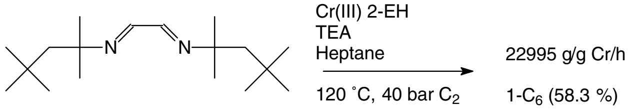
Diimine ligands. The use of diimine ligands in transition metal catalysed polymerisation of ethylene has been extensively reviewed by Ittel et al. [58]. Sumitomo Chemical Co [59] has subsequently patented the use of this class of ligands for ethylene trimerisation. Their system comprised a chromium compound, a diimine such as $R^1N{=}CR^2(CR^3R^4)_mCR^5{=}NR^6$ or $R^7R^8C{=}N(CR^9R^{10})_nN{=}CR^{11}R^{12}$ and an alkyl aluminium activator. In one example ethylene was trimerised by a catalyst system comprising Cr(III) 2-EH, glyoxalbis(1,1,3,3,-tetramethylbutylimine and TEA at molar ratios of 1:15:79 (see Scheme 14). The reaction was carried out in heptane as solvent at 40 bar ethylene pressure and 120 °C and afforded a reaction mixture containing 12.2% C_4, 72.4% C_6 (80.5% 1-C_6, 58.3% 1-C_6 overall), 1.5% C_8, 9.4% C_{10} and 3% PE. The catalyst activity was 22,995 g/g Cr per hour.

Performing the reaction under the same conditions as above, but with the addition of 15 molar equivalents of *n*-butyl bromide, improved the C_6 selectivity to 81.6% (79.8% 1-C_6). The catalyst activity, however, decreased to 16,849 g/g Cr per hour. This effect has been observed with other trimerisation catalysts [20,25,33].

A number of different compounds were also evaluated as additives including 1,2-bis (diphenylphosphino)ethane, triethyl phosphite, tetraethoxysilane and bisphenol A. These additives, however, afforded no benefits in terms of either catalyst activity or selectivity.

As with the Sasol Technology Cp-based system discussed earlier [33], this system gives low 1-C_6 selectivity within the C_6 fraction. As mentioned previously, this is problematic from a process point of view due to the difficult separation of 1-hexene from the internal isomers.

Silyl substituted nitrogen ligands. An unusual ethylene trimerisation catalyst system comprising a chromium source and metal hydroxyl compounds activated by trialkyl aluminiums was patented by Mitsubishi Corporation in the late 1990s [60]. In one example ethylene was oligomerised in heptane in the presence of TEA, $Cr(N(SiMe_3)_2)_3$ and a second catalyst precursor. This precursor was prepared by the reaction of *N*-(2,6-diisopropylphenyl-*N*-(trimethylsilyl)aminosilanetriol with TEA in hexane/THF under reflux for 3 h. The reaction was carried out at 100 °C and 35 bar ethylene pressure for 30 min to give a mixture containing 14.1% C_4, 84.5% C_6 (89% 1-C_6, 75.2% 1-C_6 overall), 0.3% C_8 and 1.1% C_{10+} (see Scheme 15). No PE formation was reported and the catalyst activity was 1066 g 1-C_6/g Cr per hour (1421 g/g Cr per hour).



Scheme 14.

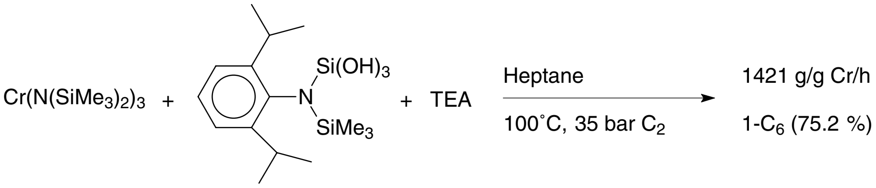
In summary, although a wide variety of catalyst systems using ligands based on nitrogen donors have been patented or published, only a handful of these systems are sufficiently active and selective to be considered as candidates for a commercial process. One such candidate is the [tris(3,5-dimethyl-1-pyrazolyl)methane]-$CrCl_3$/MAO system due to its good activity and excellent selectivity toward 1-C_6.

2.2.3. Ligands based on phosphorus donors

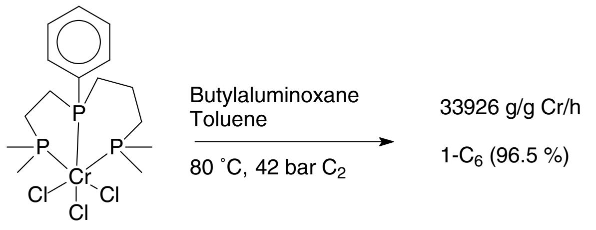
Polydentate phosphine ligands. Amoco Corporation [61] developed an ethylene trimerisation catalyst comprising chromium complexes of polydentate phosphines described by the general formula, $R_2P(CH_2)_nP(R')(CH_2)_mPR_2$, activated by an aluminoxane co-catalyst. X-ray structural analysis of the chromium complexes revealed an octahedral geometry of the complexes with meridional arrangement of the ligand, distinguishing these systems from the facially co-ordinating triazocycloalkane and tris(pyrazolyl) methane ligands discussed in the previous section.

The best catalytic results were obtained using a chromium complex of the unsymmetrical ligand, (2-dimethylphosphinoethyl)(3-dimethylphosphinopropyl)phenylphosphine. This procatalyst in toluene, when activated by 214 equivalents of butylaluminoxane (BuAO) at 42 bar ethylene pressure and 80 °C, afforded 1% C_4, 97.7% C_6 (98.8% 1-C_6, 96.5% 1-C_6 overall), 1% C_{10} and 0.3% PE (see Scheme 16). The catalyst activity was 33,926 g/g Cr per hour.

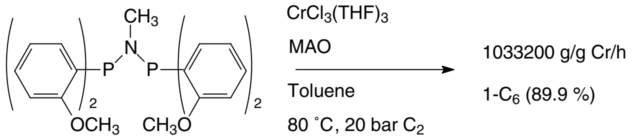
Some interesting features of the system include the fact that symmetrical ligands such as $MeP[(C_3H_6)PEt_2)]_2$ and $PhP[(C_3H_6)PMe_2)]_2$ appear to form catalysts which lose their activity over a short period of time (20 min). In addition to this, operating the catalyst system as a separate 3-component system, as opposed to starting with a preformed complex of chromium, not only lowered the



Scheme 15.



Scheme 16.



Scheme 17.

trimerisation activity but also significantly increased PE formation from <1% to ca. 12%. Ethylene was found to provide a protective effect on the activated catalyst at temperatures higher than 55 °C and increasing the ethylene pressure increased both the reaction rate and 1-C_6 selectivity.

Further distinguishing features of these catalyst systems were the exceptionally high 1-hexene selectivities and low PE (typically <2%) contents of reaction mixtures. It was even suggested that the 1-hexene obtained could be used without further purification, a very important process benefit. This is in stark contrast to many of the previous trimerisation catalysts (Phillips, etc.) which yielded product mixtures requiring fractionation of the 1-C_6 from the higher oligomeric products (especially C_{10}'s). A negative feature is the high cost of these PPP ligands which requires a difficult synthetic route involving the use of radical chemistry.

2.2.4. Ligands based on mixed P and N donors

Diphosphazane ligands – ($R_2PN(R)PR_2$). Diphosphazane ligands have previously been applied as complexes of Pd to give ethylene/CO co-polymerisation catalysts [62] and as complexes of Ni to give ethylene polymerisation catalysts [63]. British Petroleum has recently patented [64] and published [65] the first chromium-based ethylene trimerisation systems with diphosphazane ligands of the type $Ar_2PN(Me)PAr_2$ where Ar is an *o*-methoxy-substituted aryl group. When activated with MAO these systems provide extremely active and selective ethylene trimerisation catalysts.

The best trimerisation results were obtained using very low Cr and ligand concentrations. In one example, ethylene was trimerised over a 1 h period at 80 °C and 20 bar using 0.0025 mmol $CrCl_3(THF)_3$ and (2-methoxyphenyl)$_2$PN(Me)P(2-methoxyphenyl)$_2$ in 500 ml toluene. When activated by 300 equivalents of MAO, the catalyst gave 90% C_6 (99.9% 1-C_6, 89.9% 1-C_6 overall), 1.8% C_8's and 8.5% C_{10}'s. No PE formation was reported and the catalyst activity was an unprecedented 1,033,200 g/g Cr per hour (see Scheme 17), some two orders of magnitude greater than many previously reported systems. In addition to this, the decay in catalyst activity was less than 10% per hour, which is also in stark contrast to most other ethylene trimerisation systems which seem to lose most of their activity over a 30 min period. These high catalyst activities and slow deactivation rates have important process implications in that the consumption of transition metal catalyst is low and no catalyst separation step from the products before further use would be necessary.

In all the catalysis examples reported, the 1-C_6 selectivity within the C_6 fraction exceeded 99% and remarkably, no PE formation was reported. This also has major beneficial implications for the commercialisation of a process based on these systems.

This trimerisation system could also be successfully supported on silica with no loss in activity or selectivity. In fact it was even suggested that the supported catalysts lose less of their activity over time than their homogeneous counterparts. Using $CrCl_3(THF)_3$, PNP ligand and MAO on silica which had been calcined at 200 °C and reaction conditions of 8 bar ethylene pressure and 80 °C, a catalyst activity of 90,400 g/g Cr per hour was achieved, yielding 86.2% C_6's (99.8% 1-C_6, 86% 1-C_6 overall), 0.5% C_8 and 9% C_{10}'s.

As with many ethylene trimerisation catalysts, a second order dependence of catalyst activity on ethylene pressure was observed and the authors concluded that the classical metallocycle mechanism (see Section 6.1) was operative. Consistent with this, addition of 1-butene led to increased yields of octene isomers. In addition to this, experiments which were carried out for longer periods of time led to an increased yield of decene isomers relative to C_6.

Initially the authors reasoned that steric bulk in the ortho position is important in establishing catalyst performance. However, they found that an *o*-ethylphenyl PNP analogue gave no catalytic activity under the reaction conditions employed. The *p*-methoxy analogue was also inactive leading them to postulate that the potential for *o*-methoxy groups to act as pendant donors is an important factor. Ligands with *o*-methoxy substituents, having carbon instead of nitrogen bridges also gave no catalytic activity.

The authors stressed that these trimerisation systems are highly suited for tandem trimerisation co-polymerisation catalysis due to their high productivity and kinetic profile characteristics. The patent provides two such examples of tandem catalysis with the new trimerisation system, one using a Ziegler Natta polymerisation catalyst and the other using a zirconocene polymerisation catalyst. In both cases, NMR spectroscopy showed the presence of butyl branches, indicating co-polymerisation of ethylene and 1-hexene.

A few additional interesting observations regarding this system were reported. Firstly the catalyst system does not trimerise higher olefins such as 1-hexene and secondly the catalysis in the presence of hydrogen led to increased activity but not increased selectivity.

Bis-phosphinoamine ligands – ($R_2PCH_2CH_2NHCH_2CH_2PR_2$). Sasol Technology has recently patented [66] and published [67] results on a trimerisation catalyst based on Cr(III) complexes of tridentate ligands of the type $R_2PCH_2CH_2N(H)CH_2CH_2PR_2$.

The complexes are prepared by reaction of the bisphosphino amine ligands with $CrCl_3(THF)_3$ at room temperature (see Scheme 18). When activated with MAO, they are very active and selective for the production of 1-C_6. Initial attempts to improve the activity of the system centred on the modification of the R groups on the phosphorous atoms. Highly basic, but sterically demanding dicylcohexylphosphino moieties led to decreased activity and increased PE production. In contrast, basic but less sterically demanding diethylphosphino moieties led to increased activity and excellent 1-C_6 selectivities. The best activity was achieved using [bis-(2-diethylphosphino-ethyl)amine]$CrCl_3$, which when activated by 850 equivalents of MAO at 100 °C and 40 bar ethylene pressure, afforded a reaction mixture containing 94% C_6 (99.1% 1-C_6, 93.2% 1-C_6 overall) and 2.1% PE (see Scheme 19). NMR analysis revealed that no 1-C_6 was incorporated into the PE backbone. The catalyst activity was 37,400 g/g Cr per hour.

Catalysis examples giving as high as 97% overall 1-hexene selectivity were also demonstrated, albeit at much lower catalyst activity. Catalytic runs at different temperatures revealed that the system was more stable at 80 °C than 100 °C, whereas extended run times revealed that the catalyst deactivated dramatically over time.

Crystal structures were obtained for the [bis-(2-dicyclohexylphosphino-ethyl)amine]$CrCl_3$ and [bis-(2-diphenylphosphino-ethyl)amine]$CrCl_3$ complexes revealing a distorted octahedral geometry with meridional arrangement of the ligand.

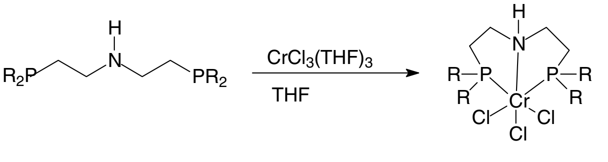
Comparing the BP PNP system with the Sasol Technology bisphosphino amine system, it is apparent that the Sasol Technology system is capable of higher overall 1-hexene selectivities (97% vs. 90% overall 1-C_6), even though it is much less active.

2.2.5. Ligands based on mixed S and N donors:

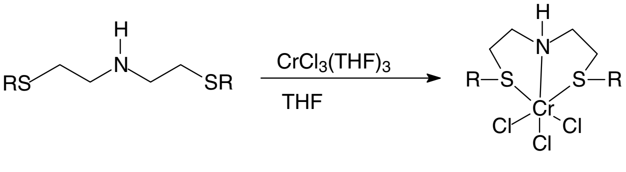
Bis-sulphanylamine ligand – ($RSCH_2CH_2NHCH_2CH_2SR$). In searching for alternatives to P-based ligands, the above-mentioned authors [68,69] reasoned that, since the phosphine pendents of the PNP system described above act as soft donor atoms capable of facile association–dissociation equilibria, the donor properties of thioether groups should be similar. Initially, alkyl SNS ligands with low steric demand were targeted due to the fact that these substituents on the PNP systems described above gave good results. The SNS ligands were prepared in good yields using inexpensive reagents and reacted with $CrCl_3(THF)_3$ at room temperature to give the corresponding [bis-(2-alkylsulphanyl-ethyl)-amine]$CrCl_3$ complexes in high yields (see Scheme 20).

An ethylene trimerisation reaction at 90 °C and 40 bar ethylene, using the [bis-(2-decylsulphanyl-ethyl)-amine]$CrCl_3$ complex activated by 280 equivalents of MAO, afforded 98.4% C_6 (99.7% 1-C_6, 98.1% 1-C_6 overall) (see Scheme 21). Only 0.16% PE was produced and the catalyst activity was 160,840 g/g Cr per hour.

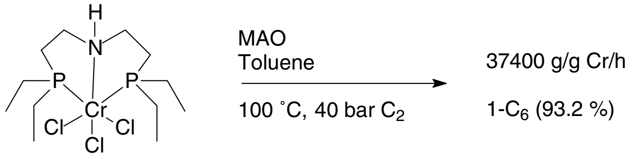
These results were superior to those obtained using the less soluble [bis-(2-ethylsulphanyl-ethyl)-amine]$CrCl_3$ complex. More importantly, it was found that the more soluble complexes could be activated with very



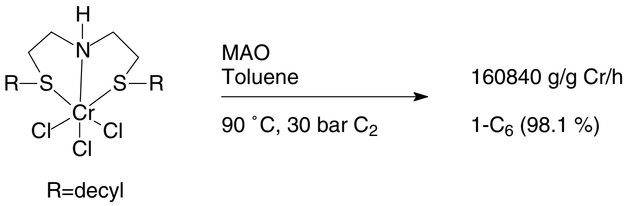
Scheme 18.



Scheme 20.



Scheme 19.



Scheme 21.

low amounts of MAO (30–100 equivalents). Due to the high cost of MAO, this has positive implications for the process economics.

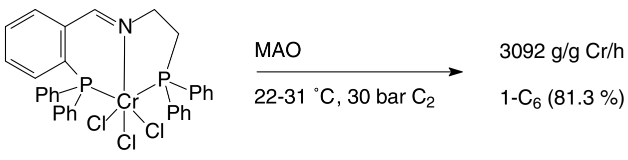
A crystal structure of [(bis-(2-ethylsulphanyl-ethyl)amine)]$CrCl_3$ was obtained and displayed the expected octahedral geometry with meridional arrangement of the ligand. Comparison of chelate bite angles and metal–ligand bond distances of the PNP and SNS systems revealed that they were very similar for the two systems, further supporting the author's supposition that the thioether group can be an effective substitute for the phosphine donor group in certain circumstances.

In summary, extremely active and selective catalysts based on SNS ligands were described and the authors showed for the first time the potential of sulphur-based ligands on early transition metals for olefin oligomerisation. In addition to the high activities and selectivities (in excess of 97%) achievable, the authors also demonstrated that these trimerisation catalysts could be activated with as low as 30 equivalents of MAO. The inexpensive ligands coupled with low MAO requirements and high activity and selectivity of these systems also make them potential candidates for a commercial process to 1-hexene.

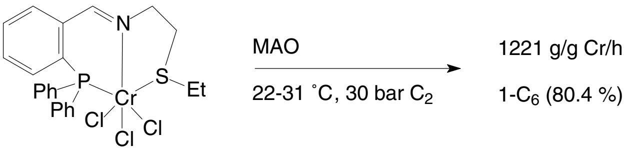
2.2.6. Ligands based on mixed PNP and PNS imines

Bluhm et al. [70] have recently reported ethylene trimerisation results using Cr(III) complexes of mixed N, P, O and S containing imines and amines. Crystal structure analyses of these complexes, as with the systems developed by Amoco [61] and Sasol Technology [67,68], revealed an octahedral geometry with meridional arrangement of the ligand. When activated by MAO, the catalysts either gave 1-hexene in reasonable selectivity (albeit at low activity), or produced mainly PE. The best trimerisation catalyst was obtained when a PNP imine complex was reacted with 100 molar equivalents of MAO at 22–31 °C and 30 bar ethylene pressure to afford 83% C_6 (98% 1-C_6, 81.3% overall 1-C_6) and 17% PE (see Scheme 22). The catalyst activity was 3092 g/g Cr per hour.

In another catalysis example the PNS imine complex was activated with 100 equivalents of MAO at 22–31 °C and 30 bar ethylene to give 82% C_6 (98% 1-C_6, 80.4% 1-C_6 overall) and 18% PE (see Scheme 23). In this case, the catalyst activity was somewhat lower at 1221 g/g Cr per hour.



Scheme 22.



Scheme 23.

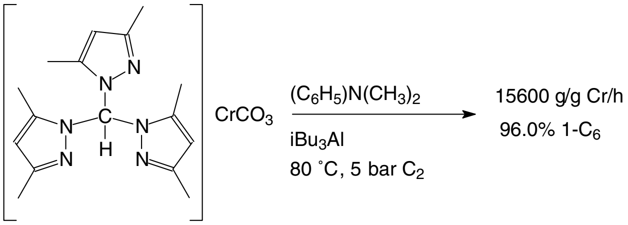
The amine equivalents of the above complexes under the same catalytic conditions were found to give mainly PE.

3. Cr(0) catalyst systems

All the chromium-based trimerisation catalysts that have been discussed up to now contain Cr^{2+} and Cr^{3+} precursors. This begs the question whether trimerisation catalysts based on Cr(0) exist. Tosoh Corporation indeed developed a number of such Cr(0)-based systems near the turn of the century. All these Tosoh systems are based on chromium tricarbonyl precursors and use triisobutyl aluminium as cocatalyst. These catalysts are generally activated by irradiation with UV light. A wide variety of compounds have been shown to be effective ligands for such catalysts. These include sulphur compounds such as dibutylsulphide [71], ethers [72], isonitriles [72], tris(3,5-dimethyl-1-pyrazolyl)methane [73–76], bis(diphenylphosphinoethyl)phenylphosphine [77] and 1,3,5-tris-(diphenylamino)benzene [78].

Although most of these Cr(0) catalysts are fairly selective towards 1-hexene, they generally exhibit very low catalyst activities. There are a few exceptions though. The most prominent of them is a catalyst prepared using tricarbonyl(1,3,5-trimethylbenzene)chromium, dibutyl sulphide and triisobutylaluminium in molar ratios of 1:10:20. This yielded a catalyst activity of 70,900 g/g Cr per hour at 80 °C and 40 bar. The product mixture contained 92.8% liquid oligomer which consisted of 92.2% C_6 (99.4% 1-C_6, 85% overall 1-C_6).

It is also possible to obtain higher selectivities towards 1-hexene, albeit at the expense of catalyst activity. Thus ethylene was trimerised in the presence of tris(3,5-dimethyl-1-pyrazolyl)methanechromium tricarbonyl, *N*,*N*-dimethylaniline and triisobutylaluminium (in molar ratios of 1:10:120) at 80 °C and 5 bar to yield >99.9%



Scheme 24.

liquid oligomers. The liquid product contained 97% C_6, 99.1% of which was 1-C_6 and 96% overall 1-C_6 (see Scheme 24). A catalyst activity of 15,600 g/g Cr per hour was achieved.

4. Heterogeneous trimerisation systems based on chromium

All the systems discussed thus far have been homogeneous trimerisation systems based on soluble chromium complexes. A number of heterogeneous ethylene trimerisation catalyst systems also exist and will briefly be discussed. It has been mentioned that the Phillips CrO_3/SiO_2 polymerisation catalyst is capable of trimerising ethylene [48], which is co-polymerised with ethylene giving co-polymer having butyl side chains. The liquid phase of these polymerisation reactions has been shown to contain oligomeric products having high selectivity toward 1-C_6, albeit very minor.

4.1. Silica-supported $Cr[N(SiMe_3)_2]_3$/isobutylaluminoxane system

Monoi et al. have patented [79–81] and published [82] results on a heterogeneous trimerisation catalyst based on $Cr[N(SiMe_3)_2]_3$ and isobutylaluminoxane (iBAO) supported on silica. They discovered that when the system was calcined at 600 °C under a nitrogen flow, it gave an active and selective ethylene trimerisation catalyst.

A catalyst system containing 1 wt% Cr on silica, having an iBAO/Cr of 24:1 at 120 °C and 7 bar ethylene pressure gave an overall 1-hexene selectivity of 74.2% and an activity of 3170 g/mmol Cr per hour (60,966 g/g Cr per hour). In accordance with the findings of Manyik et al. [5], the addition of 1,2-dimethoxyethane (DME/Cr molar ratio = 0.25) as electron donor increased the 1-C_6 selectivity to from 74.2% to 86.4%. This increased 1-C_6 selectivity came at the expense of decene isomer formation and catalyst activity. It was postulated that the role of DME was to co-ordinate with active sites, thus suppressing by-product formation.

In the absence of the silica support, the catalyst activity decreased and it was demonstrated that the calcination temperature of the catalyst affected both its selectivity and activity.

Surprisingly, the catalyst system was found to obey first order kinetics with respect to ethylene partial pressure. Most of the ethylene trimerisation systems discussed in this review have exhibited a second order dependence on ethylene. This implies that the heterogeneous system has a different rate determining step. The reaction rate of the system also decreased with reaction time, indicating some form of catalyst deactivation.

4.2. Heterogeneous variants of homogeneous systems

A number of the homogenous Cr-based catalyst systems discussed above were also successfully supported on inorganic supports to render these catalysts heterogeneous. These include the Phillips catalyst [6,7], the Tosoh maleimidyl system [24] and the BP diphosphazane system [64,65]. However, apart from the BP system, the supported catalysts yielded considerably more PE byproducts.

5. Non chromium-based trimerisation catalysts

The main drivers for investigations into non chromium-based ethylene trimerisation systems include intellectual property considerations, potential catalyst performance improvements and last but not least, environmental concerns surrounding chromium. Both UCC [5] and Phillips Petroleum [11] appear to have had a strategy of evaluating metals other than chromium for trimerisation activity. For example, UCC tested salts of uranium, cerium, titanium, vanadium and zirconium, with only uranium giving comparable yields of 1-hexene to chromium [5]. However, no detailed experimental details were provided by UCC. On the contrary, Phillips provided considerably more experimental details which will be elaborated upon in the paragraphs that follow.

5.1. Early transition metals: groups IV and V

5.1.1. Zirconium

As part of their strategy to evaluate metals other then chromium, Phillips Petroleum [11] investigated a catalyst system comprising $Zr(acac)_2$, pyrrole and TEA in molar ratios of 1:3:22 at 80 °C and 38 bar ethylene pressure. The catalysis in cyclohexane yielded 26.8% liquid products containing 26.9% C_6 (100% 1-C_6, 7.2% overall 1-C_6) and 73.2% PE at a very low catalyst activity of 29 g/g Zr per hour.

It is well known than zirconium-based systems provide good dimerisation catalysts and that zirconocene–alkene complexes can rearrange to form zirconacyclopentane compounds [83]. Further evidence that zirconium can also form metallocyclopentane species is provided in an interesting study by Wang et al. [84] on the zirconocene catalysed oligomerisation of ethylene to form methylenecyclopentane. It is believed that these zirconacyclopentane intermediates undergo β-hydrogen elimination to yield an alkenyl hydride species which after insertion of ethylene eventually undergoes cyclisation to yield methylenecyclopentane (MCP). This is the first known example for the selective trimerisation of ethylene to a cyclic C_6 isomer, rather than the more commonly observed linear 1-hexene.

The best selectivity to MCP was achieved using Cp_2ZrCl_2 activated by 100 equivalents of TEA with the addition of a pyridine promoter at reaction conditions of 150 °C and 14 bar ethylene pressure. This gave an overall selectivity to MCP of 43%. When ethyl aluminoxane (EAO) was used as the activator (Al:Zr = 100:1) it also yielded MCP, but at lower molar equivalents (e.g. Al:Zr = 25:1), 55% 1-hexene was formed and the selectivity to MCP was only 3%. The catalyst activity was extremely low at 153 g/g Zr per hour (14 kg/mol Zr per hour). In all cases the major side products were PE and a small amount of 1,5-hexadiene.

From these results, it is clear that zirconium-based systems currently have low activity with a maximum selectivity towards 1-hexene of around 55%. Considerable quantities of PE are also produced, which from a process point of view is very problematic.

5.1.2. Vanadium

Phillips Petroleum [11] surprisingly found that a catalyst system comprising $V(O)(acac)_2$, pyrrole and TEA using molar ratios of 1:3:22 in cyclohexane at 80 °C and 38 bar ethylene yielded 56.8% liquid oligomers containing 63% C_6 (79.4% 1-C_6, 45% overall 1-C_6) and 43.2% PE with a low catalyst activity of 115 g/g V per hour.

Enichem S.P.A. [85] has subsequently also patented a selective trimerisation catalyst based on low oxidation state vanadium species described by the general formula $(arene)_2VX$ where arene = benzene or mono-, di- or trialkylsubstituted benzene, V = vanadium and X = Cl, Br, I, $B(Ar)_4^-$, $AlCl_4^-$, carboxylates and sulphonates.

Unexpectedly it was demonstrated that the catalysis could be initiated by the addition of a heterocyclic compound in a molar ratio of 1:20 (with respect to the vanadium), or even more surprisingly, without a co-catalyst at all. This heterocyclic compound could be selected from pyrroles, pyrazoles, phenanthroline and pyridine amongst others.

In the best catalytic example, $V(Mesityl)_2$ and $Cp_2Fe(BPh_4)$ were combined in a 1:1 molar ratio and the trimerisation reaction was carried out at room temperature and 7 bar ethylene pressure. This afforded a reaction mixture containing 99% 1-hexene at an activity of 605 mol ethylene/mol V per hour (333 g/g V per hour).

The fact that a co-catalyst is not essential for these vanadium systems is an attractive attribute, but from an economic viability viewpoint, higher catalyst activities would be required.

5.1.3. Tantalum

The discovery of tantalum as a trimerisation catalyst can be attributed to the detection of highly branched PE oils during the polymerisation of ethylene with $TaCl_5$ activated by an alkylaluminium halide in chlorobenzene or hexane solvent [86]. The formation of these branched oils could only be explained by a dual catalytic mechanism whereby ethylene is first oligomerised by a tantalum alkyl species to alpha olefins. These alpha olefins are further oligomerised by cationic oligomerisation by Lewis acid species.

The catalysis was then conducted in the presence of 2,6-di-*t*-butylpyridine, which is known to inhibit cationic oligomerisation by acting as a proton sponge. A catalyst comprising $TaCl_5$, ethylaluminium dichloride and 2,6-di-tert-butylpyridine in a 1:1:1 molar ratio using chlorobenzene as solvent at 45 °C and 48 bar ethylene pressure over 16 h gave a liquid oligomeric product containing 45% 1-hexene (trimerisation) and 55% 1-alkenes showing a Schulz–Flory distribution ($\alpha = 0.73$). The fact that 45% 1-hexene was detected gave credence to the dual catalytic mechanism.

It was subsequently discovered that the combination of $TaCl_5$, a trialkylaluminium and a tetraalkylammonium chloride in chlorobenzene improved the selectivity towards the trimer, giving 90% liquid product of which 75% is 1-C_6 (67.5% 1-C_6 overall) in an ethylene oligomerisation reaction.

Following on from this discovery, Andes et al. [87] then developed a highly selective 'naked' trimerisation catalyst using $TaCl_5$ and a methylating agent such as $Zn(CH_3)_2$ in a 1:1 molar ratio. The catalysis in chlorobenzene at 45 °C and 48 bar ethylene pressure gave an overall 1-C_6 selectivity of 96% with a catalyst activity of 460 mol C_2/Ta h (214 g/g Ta per hour). Various alkylating agents were found to activate this procatalyst.

It is believed that $TaCl_5$ is alkylated to form $Ta(CH_3)_2Cl_3$ which was shown by a variety of ^1H and ^2H NMR experiments to be the intermediate precursor to the active catalyst.

An interesting feature of this system is that no ligand is involved in the catalysis. The active trimerisation $Ta(III)Cl_3$ species was proposed to be 'naked' (see Section 6.3); however in all likelihood, the chlorobenzene solvent performs a co-ordinating role during the catalysis. Another interesting feature is that when $Ta(CH_3)_2Cl_3$ was used as precursor, only ethylene was required to activate the catalyst.

5.1.4. Titanium

Phillips Petroleum [11] also evaluated a system comprising $Ti(O)(acac)_2$, pyrrole and TEA at molar ratios of 1:3:22. At 80 °C and 38 bar ethylene pressure the reaction afforded 71.2% liquid oligomeric products of which 55% was C_6 (87.3% 1-C_6, 34.2% 1-C_6 overall) with a catalyst activity of 222 g/g Ti per hour.

The first hint of a truly selective titanium-based trimerisation catalyst was the dual Cp^*TiMe_3-$B(C_6F_5)_3$ system developed by Pellecchia et al. [88] for the production of branched linear low density polyethylene (LLDPE). Only butyl branching was observed in the polymer and 1-hexene was detected in high selectivity in the liquid fraction via GC and ^{1}H NMR analysis. The ability of this catalyst to behave as both a trimerisation and co-polymerisation catalyst was also observed during the co-polymerisation of ethylene with styrene [89]. 6-Phenyl-1-hexene was initially formed from ethylene and styrene and was co-polymerised with ethylene to form PE with 4-phenyl-1-butyl branches. The use of other titanium precursors such as Cp^*TiCl_3, $CpTiCl_3$ or (Ind)$TiCl_3$ with MAO resulted in the suppression of co-polymerisation and the formation of up to 90% phenyl hexene oligomers.

A polymerisation catalyst system comprising $(Cp^*)Ti(OCH_2Ph)_3$ and modified methylaluminoxane (MMAO) was found by Zhu et al. [90] to yield a mixture of ethyl and butyl branched polymers. The presence of ethyl and butyl branches could be attributed to the in situ formation of 1-butene and 1-hexene, which was subsequently co-polymerised with ethylene. A mechanism involving the formation of titanocyclopentane and titanocycloheptane intermediates was proposed by the authors to explain this selective formation of dimers and trimers.

Following on from the above discoveries, Deckers et al. [91] were able to develop the first truly active and selective non chromium-based ethylene trimerisation catalyst. The breakthrough in the design was essentially the recognition that the toluene solvent stabilised the active Ti(II) trimerisation catalyst species for the Cp^*TiMe_3-$B(C_6F_5)_3$ system [88]. The authors therefore introduced a pendant arene group onto the Cp ring to mimic this solvent stabilisation role, which proved to be the key in switching the selectivity of the catalysts from polymerisation to trimerisation. This arene pendant group is proposed to behave as a hemi-labile ligand, thereby stabilising the reactive metal centre, while at the same time maintaining its accessibility to substrate molecules.

In one catalytic example ethylene was trimerised using $[CpCMe_2Ph]TiCl_3$ and 1000 equivalents of MAO at 2 bar ethylene pressure and 30 °C, affording a reaction mixture containing 97.4% liquid oligomeric products comprising 87% C_6 (98% 1-C_6, 83% 1-C_6 overall), 1% 1-C_8, 11% C_{10} and 2.6% PE (showing no signs of 1-C_6 incorporation) (see Scheme 25). The catalyst activity was 535 g C_6/mmol Ti/bar h (22,354 g/g Ti per hour). The use of $[\eta^5\text{-}C_5H_4CMe_2Ph]TiMe_3$ as the metal precursor combined with $[PhMe_2NH][B(C_6F_5)_4]$, $B(C_6F_5)_3$ or MAO/SiO_2 also gave active and selective ethylene trimerisation catalysts.

The effect of various parameters on catalyst performance was investigated. These included the effect of (i) the hemi-labile pendant arene group; (ii) aromatic vs. aliphatic solvents; (iii) various bridges between the Cp and arene rings; (iv) substituents on the arene ring and (v) substituents on the Cp ring.

By combining the effects of the above changes, strongly non-linear additive results were observed. The most active system tested contained a CMe_2 bridge with the $SiMe_3$ substituent on the Cp and alkyl substituents on the arene rings (see Scheme 26). A subtle interplay of both steric and electronic effects between these three major parameters was thus responsible for the selective and active trimerisation behaviour.

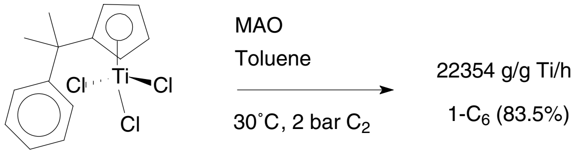
In a further modification to this titanium-based catalyst, Huang et al. [92] replaced the pendant arene with a pendant thienyl group and the resultant complexes were evaluated using 1000 equivalents MAO at 30 °C and 8 bar ethylene pressure in toluene. Two such complexes were synthesised and evaluated. However, only the complex having the thiophene moiety linked to the Cp ring via a carbon bridge at the 2-position was selective towards 1-hexene formation. This complex has the capability of either η^1-S or η^5 co-ordination to the Ti centre which seemed to be essential for selective trimerisation. The authors proposed that the η^1-S co-ordination mode favoured the stabilisation of the proposed initial Ti(II) active trimerisation species.

A catalytic run using this complex yielded 1-hexene in 86% overall selectivity with an activity of 220 kg/mol Ti per hour (4596 g/g Ti per hour) (see Scheme 27). 1-Hexene selectivities up to 95% could be achieved, but at the expense of catalyst activity.

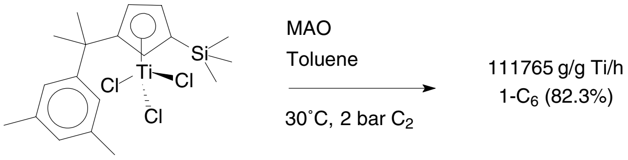
In summary, even though the titanium-based trimerisation catalysts rival the chromium-based systems with respect to activity and selectivity, one major disadvantage is the large excess of MAO required (1000 equivalents).

5.2. Late transition metals

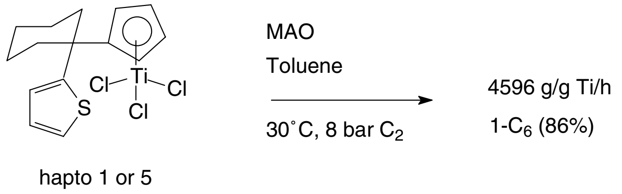
Most known ethylene trimerisation catalysts are based on early transition metals such as Cr, Ti, V and Ta. However, it is not inconceivable for the late transi-



Scheme 25.



Scheme 26.



Scheme 27.

tion metals to form active trimerisation catalysts. In support of this, some nickel-based systems have been evaluated in the patent literature.

In the first of three systems, Phillips Petroleum [11] combined Ni(acac)$_2$, pyrrole and TEA in molar ratios of 1:3:22 at 80 °C and 38 bar ethylene pressure to afford a reaction mixture containing 95.4% liquid oligomeric products of which 69% was C_6 (65% 1-C_6, 62% 1-C_6 overall). The catalyst activity was a very modest 324 g/g Ni per hour (see Scheme 28).

In another example using a Ni-based catalyst, Mitsui Chemicals [93] have shown that the combination of $NiBr_2(PhN{=}CHC_5H_4N)$ and aluminoxanes in molar ratios of 1:250 at 25 °C and 1 bar ethylene pressure afforded a liquid product containing 60% trimer, 24% dimer and 16% tetramer. The catalyst activity was 10,419 g/g Ni per hour (see Scheme 28).

A similar Ni(II) precursor, i.e. $(Ph_3P)_2NiBr_2$ could be activated by MAO [94] or $MeAlCl_2$ [95] to form a trimerisation catalyst. The best trimerisation result was achieved using this precursor and $MeAlCl_2$ in molar ratios of 1:300, under reaction conditions of 100 °C and 30 bar ethylene pressure. This gave a liquid product containing 95% trimer at an activity of 118,535 g/g Ni per hour. These trimers contained 47% 3-methyl-2-pentene, 21% 2-ethyl-1-butene and 25% 2-hexene (see Scheme 28).

5.3. Actinides

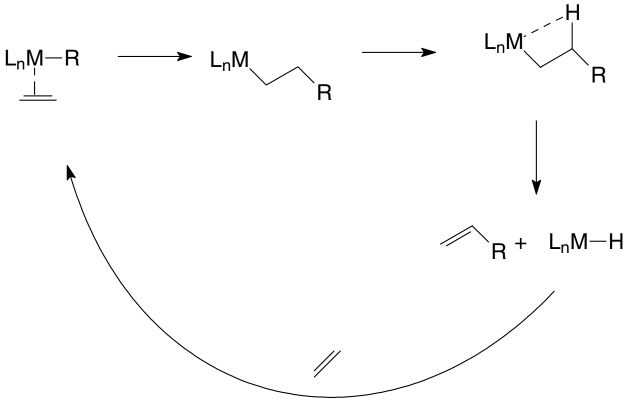
As already mentioned, Manyik et al. [4,5] reported that of all the other metal salts evaluated, only uranium alkanoates gave comparable yields of 1-hexene to chromium (see Section 1). Although no further evidence exists in the open trimerisation literature for actinide-based trimerisation systems, this report suggests that other actinide-based trimerisation systems may exist. Possible reasons why actinide systems have not received much attention to date are the cost and availability of these metal precursors.

6. Mechanistic considerations and molecular modelling

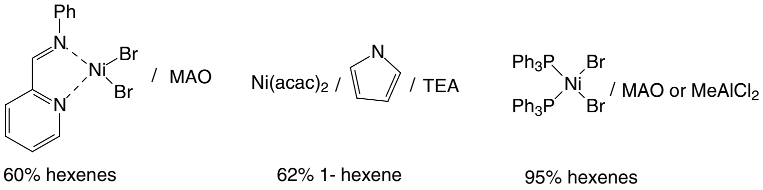
6.1. Historical development of the metallocycle mechanism

Prior to the discovery of ethylene trimerisation, the oligomerisation of ethylene to linear alpha olefins was well understood. The product distribution of the known linear alpha olefin processes usually formed a statistical series of oligomers following a Schulz–Flory [96] or Poisson distribution. According to the generally accepted mechanism proposed by Cossee and Arlman [97], chain growth occurred via ethylene co-ordination followed by insertion into a transition metal alkyl bond. Ultimately, chain termination occurred via β-hydrogen transfer to the metal to form a metal hydride species, thereby releasing a linear alpha olefin (see Scheme 29).

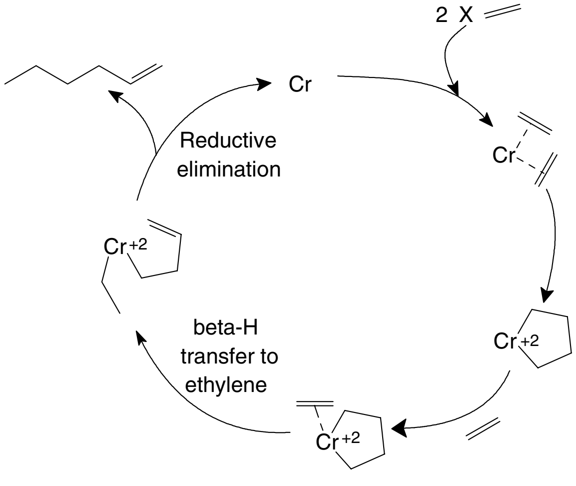
McDermott et al. [98] in the early 1970s demonstrated the existence of Pt(II) metallocycles thereby showing in principle that metallocyclic reaction intermediates could exist. This gave credence to the first metallocycle-based oligomerisation mechanism proposed in 1977 by Manyik et al. [5] for the selective chromium catalysed trimerisation of ethylene to 1-hexene (see Scheme 30). The proposed mechanism involved the co-ordination of two ethylene molecules, followed by chromacyclopen-



Scheme 29.



Scheme 28.

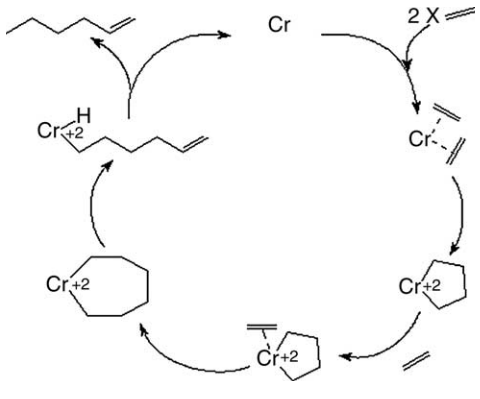


Scheme 30.

tane formation. These authors did not allow for further metallocycle growth to a larger metallocycle, but instead proposed a β-hydrogen transfer from the chromacyclopentane to a third co-ordinated ethylene to yield a chromium butenyl ethyl intermediate. 1-Hexene is liberated via a reductive elimination from this di-alkyl intermediate. Kinetic experiments conducted by these same authors indicated that the reaction was second order with respect to ethylene, and thus the formation of the chromacyclopentane was proposed as the rate-determining step.

Chromium metallocyclopentane species were also invoked in the activation of the widely known Phillips CrO_3/SiO_2 catalyst for ethylene polymerisation [31,99].

It was subsequenly postulated by Briggs [42] that, instead of a β-hydrogen transfer to ethylene, fast insertion of ethylene into the metallocyclopentane species occurs to form a metallocycloheptane. At this stage, ring opening occurs via the formation of a chromium hexenyl hydride species, which undergoes reductive elimination to liberate 1-hexene and the active catalytic species (see Scheme 31). This proposal is supported by the observations of McDermott et al. [98] in their studies on the thermal decomposition of platinocycles. Briggs stipulated that for selective liberation of 1-hexene, this insertion step must be faster than the decomposition of the metallocyclopentane to 1-butene. On the other hand, the liberation of 1-hexene must be faster than further ethylene insertion into the metallocycloheptane to form larger rings.



Scheme 31.

The authenticity of this mechanism was further established by the publication of crystal structures of five- and seven-membered chromium metallocycle species, of which the seven-membered species was shown to decompose more readily to give the corresponding alpha olefin (1-hexene) [32,100]. Stable alkyl hydride species for chromium are quite rare, but crystal structures of such species have also been reported [101]. In addition to this, Agapie et al. [102] have also provided evidence for the validity of such a metallocycle mechanism by carrying out a trimerisation reaction using a 1:1 mixture of C_2D_4 and C_2H_4. The authors reasoned that the metallocyclic route would give no H/D scrambling, while the classical Cossee-type mechanism would lead to H/D scrambling and the formation of isotopomers containing odd numbers of deuterons. As expected, addition of an equimolar mixture of C_2D_4 and C_2H_4 to a catalyst prepared by reacting $[((o\text{-MeO-Phenyl})_2P)_2NCH_3]CrPh_3$ with $H(Et_2O)B(C_6H_3(CF_3)_2)_4$ only yielded the even numbered isotopomers C_6D_{12}, $C_6D_8H_4$, $C_6D_4H_8$ and C_6H_{12} in a 1:3:3:1 ratio.

Another important aspect of the mechanism to be considered is the oxidation state of the chromium during the various stages of the catalytic cycle. Oxidative addition of the first two ethylene molecules to form a metallocyclopentane species involves an increase in the formal oxidation state from M to M^{2+}. On the other hand, 1-hexene liberation via reductive elimination involves a decrease from M^{n+2} to M^n. This is not yet well understood, but Cr(III)/Cr(V) [100], Cr(I)/Cr(III) [5,48] and Cr(II)/Cr(IV) [40,103] couples have been proposed to date.

6.2. Recent advances using molecular modelling

Although a metallocycle-based mechanism for ethylene trimerisation was already proposed in 1977 by Manyik et al. [5], the first molecular modelling studies relating to this mechanism were only published in 2003 [104–107]. This is partly due to the fact that until recently only chromium-based trimerisation systems were known, which would require notoriously challenging open shell calculations. In addition, there also existed little fundamental experimental data on both the exact nature of any Cr species in the catalytic cycle and the electronic structure of such Cr complexes to provide experimental support for theoretical studies. However, assuming a Cr(II)/Cr(IV) metallocycle couple for the Phillips catalyst, van Rensburg et al. [103] have recently published an extensive theoretical study on this system.

These authors showed that no spin state crossing occurs for the individual catalytic intermediates and that the triplet spin state is the ground state for all the possible calculated structures.

After the recent published discoveries of tantalum [87] and titanium [91] based trimerisation systems, there was an increased interest in understanding this highly selective reaction. Yu and Houk [104] performed a detailed study on the 'naked' ligand-free tantalum catalyst system, while Blok et al. [105], de Bruin et al. [106] as well as Tobisch and Ziegler [107] independently performed calculations on the half metallocene titanium catalyst system. The main driving forces for these calculations were to understand why the insertion of the third ethylene molecule into the metallocyclopentane is preferred to liberation of 1-butene and why 1-hexene liberation occurs in preference to further metallocycle growth. It is interesting to note that none of these theoretical studies even considered the mechanism proposed by Manyik et al. [5] involving a β-hydrogen transfer from the metallocyclopentane species to a third co-ordinated ethylene molecule. Other aspects that did, however, receive attention include catalyst activation, the role of hemi-labile ligands on the catalytic intermediates as well as the role of the counter ion.

6.3. Active catalyst formation

Active trimerisation catalysts are typically generated in situ by the addition of a co-catalyst, and although the individual activation steps and co-catalysts do vary from system to system, some general trends are evident. Most of these catalysts are based on transition metal salts and it is accepted that the role of the co-catalyst is to alkylate the metal [48,91]. For instance, Köhn et al. [48] provided some experimental evidence for the formation of a dinuclear chromium alkyl intermediate species containing μ-CH_3 bridges during the activation of chromium triazacyclohexane systems with MAO (see Scheme 32). Co-catalysts that are generally employed include alkylaluminium compounds ranging from trimethylaluminium (TMA) to TEA to aluminoxanes, such as MAO and EAO, as well as metal alkyl compounds such as Li, Sn and Zn alkyls.

Generally, if a transition metal alkyl source is employed instead of an alkylaluminium activator, then bulky Lewis acids or compounds containing weakly co-ordinating anions, such as $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$, are required for catalyst activation [108]. On the other hand, no co-catalyst was necessary to activate some vanadium-diaryl [85] and tantalum-dialkyl trimerisation catalysts [87], and these procatalysts could be activated directly with ethylene.

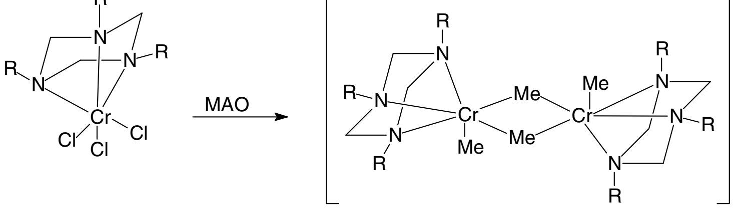
It is also believed that for some systems, the co-catalyst reduces the transition metal centre during catalyst activation [40,103].

For most catalyst systems, the in situ generated metal alkyl species can undergo ethylene insertion to give chain growth. This will especially be the case for methyl-containing species, which cannot undergo β-hydrogen transfer and elimination reactions. Such methyl-containing species will have to undergo successive ethylene insertion, β-hydrogen elimination and reductive elimination steps to generate intermediate species with two adjacent vacant sites for metallocyclopentane formation. Deckers et al. [91] did indeed propose such a pathway for the activation of $[C_5H_4C(CH_3)_2C_6H_5]TiCl_3$ with MAO to generate an active Ti(II) trimerisation catalyst via a $[C_5H_4C(CH_3)_2C_6H_5]Ti(IV)(CH_3)_2^+$ species (see Scheme 33).

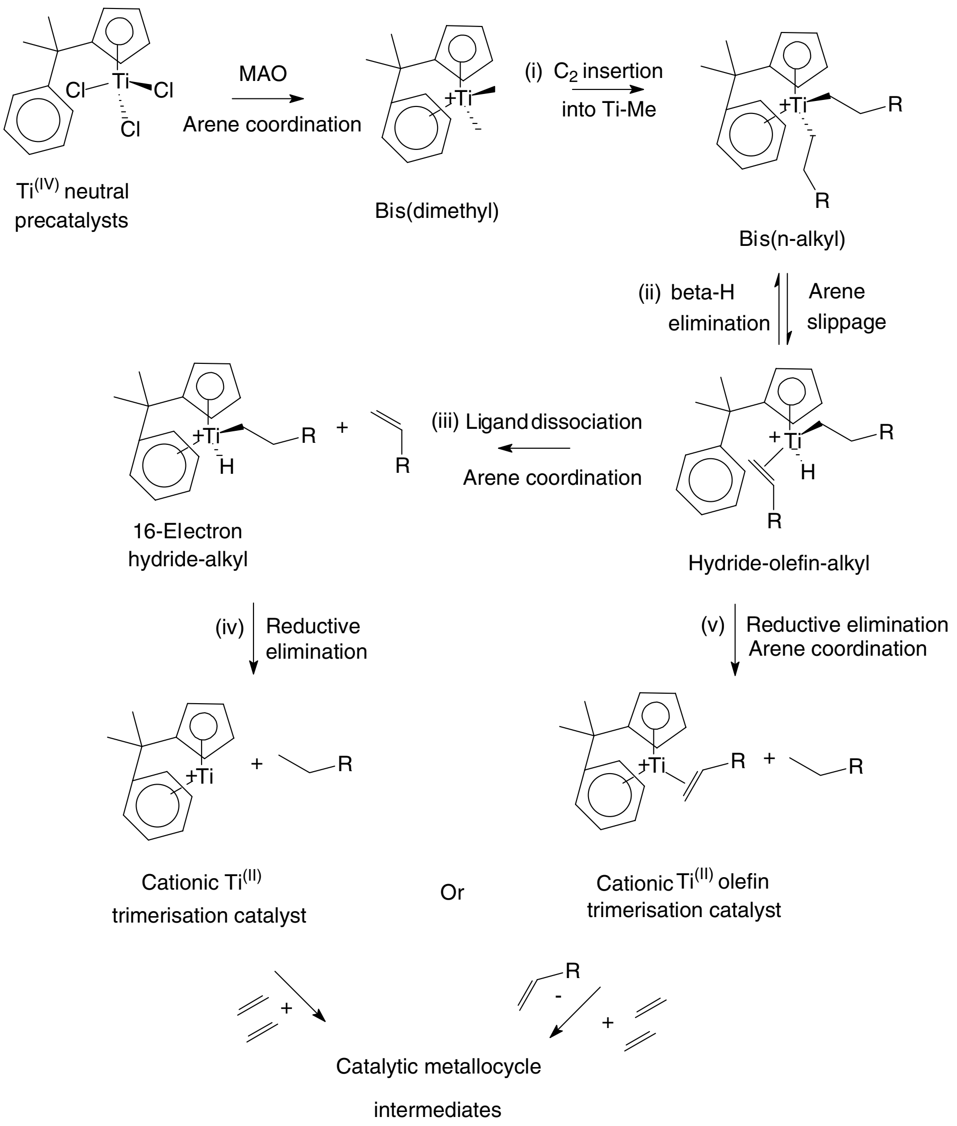
This proposed activation mechanism was later modified slightly as the result of a molecular modelling investigation by Blok et al. [105]. These authors indicated that the active Ti(II) olefin species (and the corresponding alkene and alkane) could be generated via a single agostic assisted β-hydrogen transfer step from the Ti(IV) dialkyl species without having to proceed via a hydride intermediate and subsequent reductive elimination step (see Scheme 34).

For the metal dialkyl intermediate, the direct agostic assisted transfer of the β-hydrogen of one alkyl group to the alpha-carbon of the second alkyl group was thus calculated by Blok et al. to be the lowest energy pathway. This was also confirmed to be a viable pathway by independent calculations [83,104,107].

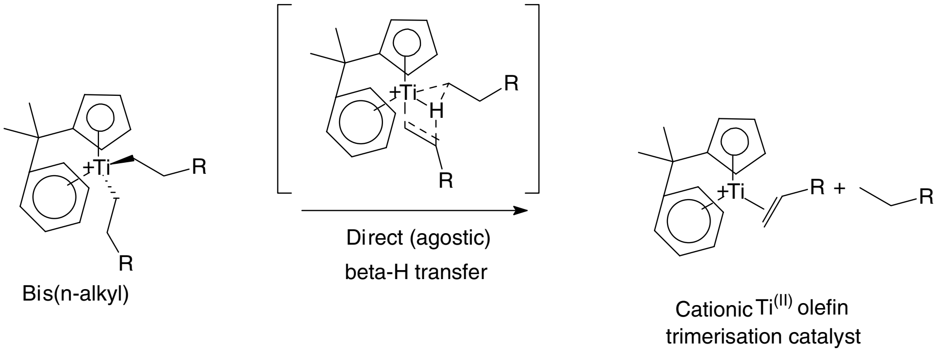
Köhn et al. [48], Agapie et al. [102] and Andes et al. [87] have provided experimental evidence for such an activation mechanism (see Schemes 31 and 32) for both chromium- and tantalum-based catalysts.



Scheme 32.



Scheme 33.

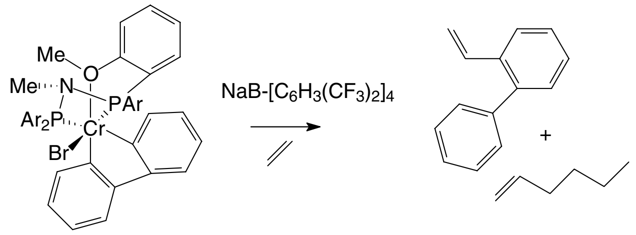


Scheme 34.

For example, as referred to above, Köhn et al. postulated that the activation of chromium triazacyclohexane systems for trimerisation of higher alpha olefins proceeds via a methyl-bridged dinuclear chromium intermediate (see Scheme 32) [48]. Insertion of the first olefin molecule (1-hexene in this case) effected the cleavage of all μ-methyl bridges. Subsequent β-hydrogen transfer and reductive elimination steps resulted in the formation of the active trimerisation catalyst, with concomitant release of methane and 2-methyl-1-hexene. The presence of small quantities of both these products in the reaction mixture was also confirmed via NMR spectroscopy.

For tantalum-based systems, Andes et al. [87] postulated that the activation of $TaCl_3(CH_3)_2$ involved the insertion of one ethylene molecule to form $TaCl_3(CH_3)(CH_2CH_2CH_3)$, followed by the formation of the metal alkene hydride intermediate $TaCl_3(CH_3)(H)(CH_3CH{=}CH_2)$ via β-hydrogen elimination. Subsequent reductive elimination of CH_4 would yield the active Ta(III) catalyst. ^{2}H NMR experiments involving the reaction of $TaCl_5$ with CD_3Li and ethylene revealed the liberation of CD_3H. In addition to this, the occurrence of odd-carbon alpha olefins in the product spectrum suggested that the produced propene was also incorporated during the oligomerisation reaction.

Finally, Agapie et al. [102] demonstrated that upon activation of $(PNP^{OMe})Cr(o,o'$-biphenyldiyl)Br with $NaB\text{-}[C_6H_3(CF_3)_2]_4$, further reaction with ethylene yielded *o*-vinylbiphenyl in addition to 1-hexene (see Scheme 35). The *o*-vinylbiphenyl formation can be explained conveniently by the consecutive ethylene insertion, β-hydrogen transfer and elimination steps.



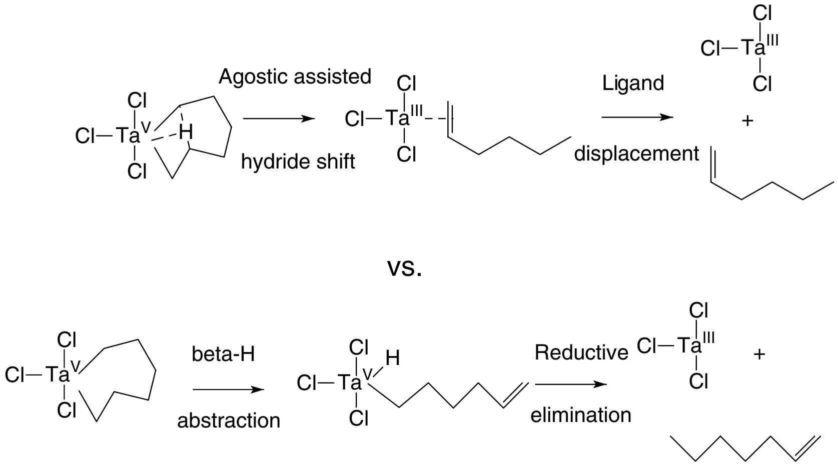
Scheme 35.

6.4. Metallocycle formation, growth and reductive elimination

As alluded to above, theoretical studies by Derat et al. [83] on acyclic metal dialkyl species highlighted the feasibility of a direct agostic assisted transfer of the β-hydrogen of one alkyl group to the alpha-carbon of the second alkyl group. In the process a reduced metal species and corresponding alkene and alkane are liberated. Similarly, Yu and Houk [104] considered such a mechanism as an alternative to the conventional two-step metallocycle decomposition mechanism postulated by Whitesides and co-workers [98] (see Scheme 36).

It was found by these authors that the concerted one-step route was favoured over the conventional two-step route, in which the reductive elimination step is particularly unfavourable. However, due to geometric constraints of the five-membered metallocycle, 1-butene cannot be liberated via such an agostic assisted β-hydride shift mechanism, and has to proceed via the two step route. This provides an effective barrier for 1-butene liberation and thus favours insertion of the third ethylene molecule. Independent calculations conducted on the Ti [105–107] and Cr [103] systems all yielded similar results. In addition, it was found for the Cr-pyrrole study that a conformational change of the ring from a chair to boat was required to facilitate the agostic-assisted β-hydrogen transfer.

Agapie et al. [102] have conducted some empirical studies using deuterated ethylene to investigate the mechanism of metallocycle collapse. It was mentioned by these authors that if an agostic-assisted hydride transfer was to occur; such a process would be expected



Scheme 36.

to involve hydrogen tunnelling and show unusual kinetic isotope effects. They concluded that the minor isotope effects observed in their experiments do not support or disprove the proposed agostic assisted mechanism.

Amongst the five above mentioned theoretical studies, opinion was divided on whether further growth of the metallocycloheptane intermediate to form larger rings and concomitantly higher oligomer products (such as 1-octene) is possible. Both Yu and Houk [104] as well as Blok et al. [105] put forward various arguments that 1-octene formation via the metallocycle mechanism is highly unlikely if not impossible. On the other hand, both de Bruin et al. [106] and Tobisch and Ziegler [107] do not discount that the continued insertion of ethylene. Tobisch and Ziegler suggest that if the rate of liberation of 1-hexene becomes equivalent to the rate of ethylene insertion into the seven-membered and large metallocycle rings, then specific olefin selectivity would be lost and a statistical distribution of oligomers, starting at 1-hexene, is to be expected.

6.5. *Kinetics/rate-limiting step*

Both Manyik et al. [5] and Yang et al. [20] reported a second order dependence on ethylene for two different chromium-based catalyst systems. These observations imply that the rate-determining step for both of these chromium-based systems is the formation of a metallocyclopentane intermediate via two co-ordinated ethylene molecules. On the contrary, Köhn et al. [48] established a first order dependence with respect to 1-hexene for the chromium triazacyclohexane systems (^{1}H NMR was used to derive a rate equation for this reaction). Similarly, Deckers et al. [91] also reported a first order dependence with respect to ethylene for the $[C_5H_4C(CH_3)_2C_6H_5]TiCl_3$ system. This would imply that the rate determining step in these systems is the insertion of an ethylene molecule into the metallocyclopentane species rather than initial metallocyclopentane formation.

However, there exist some inconsistencies between the experimental observations and the molecular modelling results on this matter. For example, van Rensburg et al. [103] calculated that the rate determining step in the mechanism for the Phillips catalyst was the growth of the chromacyclopentane to chromacycloheptane step, and not metallocyclopentane formation.

Similarly, de Bruin et al. [106] postulated that the liberation of 1-hexene from the titanacycloheptane ring, and not metallocycle growth, is the rate-limiting step for the $C_5H_4C(CH_3)_2C_6H_5]TiCl_3$-based system (although this should have exhibited a zero order dependence with respect to ethylene). This is contrary to the results of Blok et al. [105] as well as Tobisch and Ziegler [107] whose conclusions agree with the experimental results of Deckers et al. [91].

6.6. *Oxidation state of the active species*

As stated previously, in some cases the procatalyst is believed to be reduced during the catalyst activation process. After activation, the active catalyst undergoes successive reductive elimination/oxidative addition cycles. Table 1 gives a summary of the currently proposed oxidation state couples for some of the trimerisation catalyst systems.

Comparing the chromium oxidation states, Cr(III) complexes are typically stable, while Cr(II) and Cr(IV) complexes are less stable whereas Cr(V) and Cr(I) complexes are quite rare and unstable. Thus in terms of stability, the Cr(II)/Cr(IV) couple therefore seems to be the most likely. Known Cr(V) complexes typically only have oxygen or halide ligands, whereas organometallic Cr(I) complexes are possible with donor ligands such as aryl isocyanides and bipyridine [109]. The Cr(I)/Cr(III) couple thus seems to be more likely than the Cr(III)/Cr(V) couple.

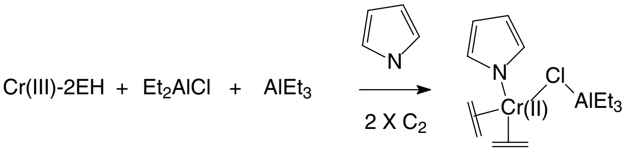
It should, however, be noted that experimental evidence using X-ray photoelectron spectroscopy of the Phillips catalyst (see Section 2.1.1) seems to indicate a Cr(I)/Cr(III) couple for this system [21].

6.7. *Role of the counter ion*

In the case of the Phillips catalyst system, the presence of halogenated compounds provides a beneficial effect which has been extensively discussed in Section 2.1.1. In an attempt to explain this observation, van Rensburg et al. [103] proposed the formation of a

Table 1
Proposed oxidation state couples for various catalysts

Couple	d-Electrons	Reference
Cr(III)/Cr(V)	d^3/d^1	Meijboom et al. [100]
Cr(II)/Cr(IV)	d^4/d^2	Theopold [31], Morgan et al. [40], van Rensburg et al. [103]
Cr(I)/Cr(III)	d^5/d^3	Köhn et al. [48], Fang et al. [21]
Ta(III)/Ta(V)	d^2/d^0	Andes et al. [87]
Ti(II)/Ti(IV)	d^2/d^0	Deckers et al. [91], Blok et al. [105], de Bruin et al. [106], Tobisch and Ziegler [107]
Zr(II)/Zr(IV)	d^2/d^0	Wang et al. [84]



Scheme 37.

$[ClAlEt_3]^-$ counter ion during the activation of the Phillips chromium pyrrole system (see Scheme 37).

Calculations performed by these authors to compare the effect of having the $[ClAlEt_3]^-$ fragment instead of the chloride group revealed that for all geometries the Cr–Cl bond is longer in Cr–$ClAlMe_3$ species than in the equivalent Cr–Cl compounds. More importantly, the presence of the $[ClAlEt_3]^-$ fragment also leads to a relatively lower activation energy requirement for the metallocyclopentane growth step. Since the authors believe that this is also the rate determining step, this result suggests that the presence of a chloroaluminate anion plays an important role in controlling the reactivity of this catalyst system.

It is well known that metallocene polymerisation catalyst precursors react with MAO to form active cationic species with MAO counter ions [108]. Analogous to this, MAO activation of many trimerisation systems may thus also lead to the formation of active cationic species, but to date no literature studies on this matter have been published.

6.8. Hemi-labile ligand effect

In homogeneous catalysis, hemi-labile ligands perform a dual function by stabilising the reactive metal centre, while at the same time maintaining its accessibility to substrate molecules. Thus hemi-lability is intimately related to both catalyst selectivity and activity.

The pendant arene moiety of the half-metallocene titanium catalyst system modelled by Blok et al. and others [105–107] was found to behave as a hemi-labile co-ordinating donor throughout the catalytic cycle, with the arene group being more strongly bound to the Ti(II) species than the T(IV) species. For the Ti(IV)dialkyl species, the arene moiety also promotes agostic assisted β-hydrogen transfer over ethylene insertion to form the active Ti(II) olefin trimerisation species preferentially. This is partly because the formed Ti(II) species is stabilised though significant back-bonding interaction with the arene moiety [105]. Similarly, there is a strong transition metal–arene interaction during the agostic assisted β-hydrogen transfer step to liberate 1-hexene.

When the pendant arene was compared to free benzene [105], it was found that the free benzene molecule binds more strongly to the titanium since it is not geometrically constrained and can position itself more closely to the titanium centre. The reduced space around the metal centre hinders ethylene insertion at all points in the catalytic cycle, thereby lowering the reaction rate.

Similarly, van Rensburg et al. [103] considered the hemi-labile nature of the pyrrole ligand in the Phillips trimerisation catalyst. According to these authors, the η^5 bonding mode is preferred for Cr(II) intermediates. This facilitates the formation of the metallocyclopentane species. Alternatively, the σ bonding mode is preferred for Cr(IV) intermediates which enables metallocycle growth and conformational changes. Interestingly enough, there is no preference for either mode during the agostic assisted β-hydrogen transfer step to liberate 1-hexene. It was therefore concluded by these authors that the facile ring slippage between these two modes facilitates the transformation of the Cr(IV) metallocycloheptane to the Cr(II)-1-hexene species.

6.9. PE formation

As alluded to above, the formation of the first metallocyclopentane reaction intermediate in the trimerisation reaction requires two vacant sites for olefin co-ordination. It is, however, quite conceivable that the PE rather originates from an alkylated species which does not have two such vacant sites (see Scheme 33).

Molecular modeling studies conducted by Blok et al. [105] based on the $(PhCH_2Cp)TiCl_3$-based catalyst (which yielded up to 6% 1-octene, 9% C_{12}-$_{24}$ and 34% PE experimentally [91]) confirmed this possibility. They postulated that the formation of relatively large quantities of PE by this catalyst may be attributed to a very small energy barrier of ca. 1 $\mathrm{kcal\,mol^{-1}}$ between the ethylene insertion step and the agostic-assisted β-hydride transfer step for the titanium dialkyl species invoked in the catalyst activation mechanism. Therefore, it is conceivable that some oligomers and/or polymer are formed before the catalyst enters into the trimerisation cycle. Separate results by Tobisch and Ziegler [107] were in agreement with these observations.

In conclusion, based on the insights provided by the recent molecular modeling studies, it is foreseeable that the fundamental understanding of ethylene trimerisation chemistry will accelerate. However, the lack of extensive empirical data to corroborate these theoretical studies is a matter of concern.

7. Conclusions and future outlook for selective olefin oligomerisation

The best reported trimerisation results for both chromium and non chromium-based catalyst systems are summarised in Tables 2 and 3. While it must be born in mind that some of these systems were unoptimised and that the results were obtained under varying reac-

Table 2
Chromium-based trimerisation systems

No.	Metal precursor(s)	Ligand	Activator	Ref.	Activity g/g Cr per hour	Overall 1-C6 or trimer (%)
1	Cr(III) 2-EH	DME	PIBAO	[42]	2086	74
2	Cr(II) 2-EH	DME	Al *t*-butoxide	[44]	5298	84
3	Cr(III) 2-EH	DME	Al *t*-butoxide/iBu$_3$Al	[45]	6970	82
4	Cr(III) 2-EH	2,5-DMP	TEA/Et$_2$AlCl	[6]	156,666	93
5	Cr(III) 2-EH	2,5-DMP	TEA/C$_2$Cl$_6$	[13]	3,780,000	95.4
6	Cr(III) 2-EH	Maleimide	TEA/Et$_2$AlCl	[24]	278,000	79.6
7	Cr(III) 2-EH	Pentaphenylcyclopenta-diene	TEA	[33,34]	57,700	77.2
8	CrCl$_2$	Boratabenzene/LDA	TEA	[36]	1072	62.5
9	Cr(III) 2-EH, bis(2,6-diphenyl-phenoxy)-isobutylaluminium		TEA	[37]	3654	74.4
10	Cr(III) 2-EH, bis(2,6-diphenyl-phenoxy)-magnesium		TEA	[38]	7308	83.5
11	Cr(III) 2-EH	2,6-diphenylphenol	TEA	[39,40]	23,000	77.5
12	[1,4,7-trimethyl-1,4,7- triazacyclononane]CrCl$_3$		NHAO	[46]	12,309	33.4–37.3
13	[1,3,5-trioctyl-1,3,5- triazacyclohexane]CrCl$_3$		MAO	[50]	–	99% C18
14	[1,3,5-tri-2-EH- 1,3,5-triazacyclohexane]CrCl$_3$		MAO	[51]	166	93% C36
15	[tris(3,5-dimethyl-1-pyrazolyl)methane]CrCl$_3$		MAO	[53]	40,100	99.1
16	Cr(III) 2-EH	Glyoxalbis(1,1,3,3,-tetramethylbutylimine	TEA	[59]	22,995	58.3
17	Cr[N(SiMe$_3$)$_2$]$_3$	*N*-(2,6-diisopropylphenyl-*N*-(trimethylsilyl)aminosilanetriol	TEA	[60]	1421	75.2
18	CrCl$_3$ (PPP)		BuAO	[61]	33,926	96.5
19	CrCl$_3$ (THF)$_3$	PNP^{OMe}	MAO	[65]	1,033,200	89.9
20	CrCl$_3$[R$_2$PC$_2$PNHPC$_2$PR$_2$]		MAO	[66,67]	37,400	93.2
21	CrCl$_3$[RSC$_2$PNHPC$_2$SR]		MAO	[68,69]	160,840	98.1
22	CrCl$_3$[PNP]imine		MAO	[70]	3092	81.3
23	CrCl$_3$[PNS]imine		MAO	[70]	1221	80.4
24	Cr(CO)$_3$	tris(3,5-dimethyl-1-pyrazolyl)-methane	iBu$_3$Al	[73]	15,600	96
25	Cr[N(SiMe$_3$)$_2$]$_3$/iBuAO (heterogeneous)			[82]	60,966	74.2

Table 3
Non chromium-based trimerisation systems

No.	Metal precursor(s)	Ligand	Activator	Ref.	Activity g/g M per hour	Overall 1-C6 or trimer (%)
1	$Ni(acac)_2$	Pyrrole	TEA	[11]	324	62
2	$NiBr_2(PhN{=}CHC_5H_4N)$		MAO	[93]	10,419	60
3	$NiBr_2(PPh_3)_2$		MAO	[94,95]	118,535	95
4	Cp_2ZrCl_2		EAO	[84]	153	55
5	$V(mesityl)_2$	$Cp_2Fe(BPh_4)$		[85]	333	99
6	$TaCl_5$	R'_2R_2NCl	TEA	[86]	–	67.5
7	$TaCl_5$		$ZnMe_2$	[87]	214	96
8	$[\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3CMe_2\text{-}3,5\text{-}Me_2C_6H_3]TiCl_3$		MAO	[91]	111,765	82.3
9	$\{\eta^5\text{-}C_5H_4C[(CH_2)_5]thiophene\}TiCl_3$		MAO	[92]	4596	86

tion conditions, broad comparisons can be made between the activity and overall selectivity of the various systems.

It is evident that, since the initial discovery in which less than 1% 1-hexene was reported, trimerisation technology has developed into a perfect example of an atom efficient organic synthesis. Overall selectivities to 1-hexene in excess of 99% have been reported in some instances (see entry 15, Table 2). At the same time huge improvements in catalyst activity have been made (see entries 5 and 19, Table 2). Apart from these trimerisation systems becoming more active and selective, they are also becoming less prone to deactivation (see entry 19, Table 2). In addition to this, catalysts containing a wide variety of ligands including aromatic, heteroaromatic and multidentate ligands have been developed (see Table 2).

It is also noteworthy that the technology is no longer limited to chromium and a variety of other metals, predominantly early transition metals, have been employed (see Table 3).

In view of all that has been said in this review, it would appear that the basic requirements for developing a selective trimerisation catalyst are simply matching the correct early transition metal in the required oxidation state with a ligand having the desired electronic, steric and hemi-lability properties.

In recent times there has been increased fundamental understanding of this unusual chemical transformation despite difficulties in analysing chromium and other paramagnetic species. Researchers have also turned to molecular modelling for a better understanding of mechanistic aspects.

With the rate at which the technology is progressing one can only speculate as to the future possibilities. The overall selectivities to 1-hexene are currently so high that, apart from increasing the catalyst activity and lifetime, the future focus will in all probability be on developing more cost effective catalysts. Finally, we would speculate that the next challenge from a selectivity viewpoint would be the extension of selective oligomerisation technology to the production of other target LAOs such as 1-octene and 1-decene from ethylene.

Acknowledgement

The authors would like to express their gratitude to Sasol Technology R&D (Pty) Ltd for permission to publish this work and to the Sasol Olefin Transformations Group for their invaluable contributions. We also wish to thank Willi Keim, Peter Wasserscheid and Dave McGuinness for fruitful discussions.

References

[1] Alpha Olefins (02/03-4), PERP Report, Nexant Chem Systems.
[2] ‘Linear Alpha Olefins’, CEH Marketing Research Report, September 2000.
[3] M. Zahoor, F. Al-Sherehy, O. Alabisi, M.M. Abdillahi, M.R. Saeed, US 6184428 (Saudi Basic Industries Corporation), February 6, 2001.
[4] R.M. Manyik, W.E. Walker, T.P. Wilson, US 3300458 (Union Carbide Corporation), January 24, 1967.
[5] R.M. Manyik, W.E. Walker, T.P. Wilson, J. Catal. 47 (1977) 197.
[6] W.K. Reagan, EP 0417477 (Phillips Petroleum Company), March 20, 1991.
[7] W.K. Reagan, Symp. Prepr. Conv. Light Olefins, Div. Pet. Chem., Am. Chem. Soc. 34 (1989) 583.
[8] W.K. Reagan, J.W. Freeman, B.K. Conroy, T.M. Pettijohn, E.A. Benham, EP 0608447 (Phillips Petroleum Company), August 3, 1994.
[9] R.D. Knudsen, J.W. Freeman, M.E. Lashier, US 5,563,312 (Phillips Petroleum Company), October 8, 1996.
[10] J.W. Freeman, J.L. Buster, R.D. Knudsen, US 5,856,257 (Phillips Petroleum Company), January 5, 1999.
[11] W.K. Reagan, J.W. Freeman, B.K. Conroy, T.M. Pettijohn, E.A. Benham, US 5,451,645 (Phillips Petroleum Company), September 19, 1995.
[12] E. Tanaka, H. Urata, T. Oshiki, T. Aoshima, R. Kawashima, S. Iwade, H. Nakamura, S. Katsuki, T. Okanu, EP 0 611 743 (Mitsubishi Chemical Corporation), August 24, 1994.
[13] Y. Araki, H. Nakamura, Y. Nanba, T. Okanu, US 5,856,612 (Mitsubishi Chemical Corporation), January 5, 1999.
[14] M. Tamura, K. Uchida, Y. Ito, K. Iwanaga, EP 0 614 865 (Sumitomo Chemical Company), September 14, 1994.

[15] H. Maas, S. Mihan, R. Kohn, G. Seifert, J. Tropsch, WO 2000058319 (BASF Aktiengesellschaft), October 5, 2000.

[16] H. Sato, H. Nakajima, JP 06329562 (Idemitsu Chemical Company), November 29, 1994.

[17] G. Wang, M. Xie, S. Wang, J. Qu, J. Zhao, B. Zhang, Q. Chen, Z. Yuan, X. Han, L. Li, CN 1294109 (Chinese Petroleum Group), May 9, 2001.

[18] J.T. Dixon, J.J.C. Grove, A. Ranwell, WO 01/83447 (Sasol Technology (Pty) Ltd), November 8, 2001.

[19] J. Sui, X. Du, T. Li, Hecheng Shuzhi Ji Suliao 18 (2) (2001) 23.

[20] Y. Yang, H. Kim, J. Lee, H. Paik, H.G. Jang, Appl. Catal. A 193 (2000) 29.

[21] Y. Fang, Y. Liu, Y. Ke, C. Guo, N. Zhu, X. Mi, Z. Ma, Y. Hu, Appl. Catal. A 235 (2002) 33.

[22] J.T. Dixon, J.J.C. Grove, A. Ranwell, WO 01/38270 (Sasol Technology (Pty) Ltd), May 31, 2001.

[23] A. Ranwell, M. Tshamano, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids: Industrial Applications to Green Chemistry, ACS Symposium Series, vol. 818, American Chemical Society, Washington, DC, 2002, pp. 147–160.

[24] T. Aoyama, H. Mimura, T. Yamamoto, M. Oguri, Y. Koie, JP 09176299 (Tosoh Corporation), July 8, 1997.

[25] H. Mimura, T. Aoyama, T. Yamamoto, M. Oguri, Y. Koie, JP 09268133 (Tosoh Corporation), October 14, 1997.

[26] H. Mimura, T. Aoyama, T. Yamamoto, M. Oguri, Y. Koie, JP 09268134 (Tosoh Corporation), October 14, 1997.

[27] H. Mimura, T. Aoyama, T. Yamamoto, M. Oguri, Y. Koie, JP 09268135 (Tosoh Corporation), October 14, 1997.

[28] T. Aoyama, T. Yamamoto, H. Mimura, M. Oguri, Y. Koie, JP 10007681 (Tosoh Corporation), January 13, 1998.

[29] M. Okuri, H. Okada, Y. Koie, JP 10036432 (Tosoh Corporation), February 10, 1998.

[30] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428 and references therein.

[31] K.H. Theopold, Eur. J. Inorg. Chem. (1998) 15.

[32] (a) R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, G.P.J. Verhovnik, Organometallics 16 (1997) 1511;
(b) P.W. Jolly, Acc. Chem. Res. 29 (1996) 544.

[33] H. Mahomed, A. Bollmann, J. Dixon, V. Gokul, L. Griesel, C. Grove, F. Hess, H. Maumela, L. Pepler, Appl. Catal. A 255 (2003) 355.

[34] J.J.C. Grove, H.A. Mahomed, L. Griesel, WO 03/004158 (Sasol Technology (Pty Ltd), June 27, 2002.

[35] J.S. Rogers, G.C. Bazan, Chem. Commun. (2000) 1209.

[36] T. Aoshima, T. Urata, JP 11181016 (Mitsubishi Chemical Industries), July 6, 1999.

[37] D.C. Commereuc, R.M. Drochon, C. Saussine, US 6031145 (Institut Francais du Petrole), June 17, 1998.

[38] D.C. Commereuc, R.M. Drochon, C. Saussine, EP 1110930 (Institut Francais du Petrole), June 27, 2001.

[39] D.H. Morgan, J.J.C. Grove, B.C.B. Bezuidenhout, S.L. Schwikkard, WO 02/083306 (Sasol Technology (Pty) Ltd), 12 April 2001.

[40] D.H. Morgan, S.L. Schwikkard, J.T. Dixon, J.J. Nair, R. Hunter, Adv. Synth. Catal. 345 (2003) 939–942.

[41] J.R. Briggs, US 4668838 (Union Carbide Corporation), May 26, 1987.

[42] J.R. Briggs, Chem. Commun. 11 (1989) 674.

[43] I.J. Levine, F.J. Karol, US 4777315 (Union Carbide Corporation), October 11, 1988.

[44] H. Sato, S. Suzuki, JP 07215896 (Idemitsu Chemical Company), August 15, 1995.

[45] K. Kodoi, H. Sato, JP 08183746 (Idemitsu Chemical Company), July 16, 1996.

[46] F.J. Wu, EP 0537609 (Albemarle Corporation), July 10, 1992.

[47] R.D. Köhn, G. Kociok-Köhn, Angew. Chem. Int. Ed. 33 (18) (1994) 1877.

[48] R.D. Köhn, M. Haufe, S. Mihan, D. Lilge, Chem. Commun. (2000) 1927–1928.

[49] J.P. Hogan, J. Polym. Sci. A 8 (1970) 2637.

[50] R.D. Köhn, M. Hauffe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (23) (2000) 4337–4339.

[51] P. Wasserscheid, S. Grimm, R. Köhn, M. Haufe, Adv. Synth. Catal. 343 (8) (2001) 814–818.

[52] D.L. Reger, Comments Inorg. Chem. 21 (1999) 1–28.

[53] T. Yoshida, T. Yamamoto, H. Okada, H. Murakita, US2002/0035029 (Tosoh Corporation), March. 21, 2002.

[54] M. Oguri, T. Yamamoto, H. Mimura, H. Okada, O. Yoshida, JP 2001009290 (Tosoh Corporation), January 16, 2001.

[55] M. Oguri, H. Mitsumura, H. Okada, JP 200229241 (Tosoh Corporation), August 22, 2000.

[56] T. Yamamoto, M. Oguri, H. Okada, S. Murakita, O. Yoshida, JP 2001096164 (Tosoh Corporation), April 10, 2001.

[57] O. Yoshida, H. Okada, T. Yamamoto, H.Okada, H. Murakita, JP 2002205960 (Tosoh Corporation), July 23, 2002.

[58] S. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[59] K. Iwanaga, M. Tamura, GB 2314518 (Sumitomo Chemical Company), June 27, 1997.

[60] T. Aoshima, T. Urata, JP 11222445 (Mitsubishi Chemical Industries), August 17, 1999.

[61] F.J. Wu, US 5811618 (Amoco Corporation), August 25, 1995.

[62] S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass, M.D. Jones, Chem. Commun. (2001) 699.

[63] N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen, P.G. Pringle, Organometallics 20 (2001) 4769.

[64] D.F. Wass, WO 02/04119 (BP Chemicals Ltd), January 17, 2002.

[65] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, Chem. Commun. (2002) 858–859.

[66] J.T. Dixon, J.J.C. Grove, P. Wasserscheid, D.S. McGuinness, F.M. Hess, H. Maumela, D.H. Morgan, A. Bollmann, WO 03053891 (Sasol Technology (Pty) Ltd), December 20, 2001.

[67] D.S. McGuinness, P. Wasserscheid, W. Keim, J.T. Dixon, J.J.C. Grove, C. Hu, U. Englert, Chem. Commun. (2003) 334.

[68] D.S. McGuinness, P. Wasserscheid, W. Keim, D.H. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F.M. Hess, U. Englert, J. Am. Chem. Soc. 125 (2003) 5272.

[69] J.T. Dixon, P. Wasserscheid, D.S. McGuinness, F.M. Hess, H. Maumela, D.H. Morgan, A. Bollmann, WO 03053890 (Sasol Technology (Pty) Ltd), December 20, 2001.

[70] M. Bluhm, O. Walter, M. Döring, Poster 126 at the XXXVII Jahrestreffen Deutscher Katalytiker, 17–19 March 2004 held in Weimar, Germany.

[71] M. Oguri, H. Mimura, T. Aoyama, H. Okada, Y. Koie, JP 11092407 (Tosoh Corporation), April 6, 1999.

[72] M. Oguri, H. Mimura, T. Aoyama, H. Okada, Y. Koie, JP 11092408 (Tosoh Corporation), April 6, 1999.

[73] H. Mimura, M. Oguri, H. Okada, JP 2000176291 (Tosoh Corporation), June 27, 2000.

[74] H. Mimura, M. Oguri, T. Yamamoto, H. Murakita, H. Okada, T. Yoshida, US 6,337,297 (Tosoh Corporation), January 8, 2002.

[75] M. Oguri, H. Mimura, H. Okada, JP 2000202299 (Tosoh Corporation), July 25, 2000.

[76] M. Mimura, M. Oguri, T. Yamamoto, H. Okada, Y. Osamu, JP 2001002724 (Tosoh Corporation), January 9, 2001.

[77] M. Oguri, T. Yamamoto, H. Mimura, H. Okada, Y. Osamu, JP 2001002725 (Tosoh Corporation), January 9, 2001.

[78] S. Murakita, T. Yamamoto, H. Okada, Y. Osamu, JP 2001149788 (Tosoh Corporation), June, 5, 2001.

[79] H. Monoi, H. Torigoe, M. Fushimi, M. Yamamoto, JP 09020692 (Showa Denko Chemical Company), January 21, 1997.

[80] H. Monoi, H. Torigoe, M. Fushimi, M. Yamamoto, JP 09020693 (Showa Denko Chemical Company), January 21, 1997.

[81] H. Monoi, H. Torikoshi, M. Yamamoto, JP 10060043 (Japan Polyolefin Chemical Company), March 3, 1998.

[82] H. Monoi, Y. Sasaki, J. Mol. Catal. A 187 (2002) 135–141.

[83] E. Derat, J. Bouquant, P. Bertus, J. Szymoniak, S. Humbel, J. Organomet. Chem. 664 (2002) 268 and references therein.

[84] M. Wang, Y. Shen, M. Qian, R. Li, R. He, J. Organomet. Chem. 599 (2000) 143.

[85] R. Santi, A.M. Romano, M. Grande, A. Sommazzi, F. Masi, A. Proto, WO 01/68572 (Enichem S.P.A), September 20, 2001.

[86] S. Murtuza, S.B. Harkins, G.S. Long, A. Sen, J. Am. Chem. Soc. 122 (2000) 1867.

[87] C. Andes, S.B. Harkins, S. Murtuza, K. Oyler, A. Sen, J. Am. Chem. Soc. 123 (2001) 7423.

[88] C. Pellecchia, D. Pappalardo, G. Gruter, Macromolecules 32 (1999) 4491.

[89] C. Pellecchia, D. Pappalardo, L. Oliva, M. Mazzeo, G. Gruter, Macromolecules 33 (2000) 2807.

[90] F. Zhu, Y. Huang, Y. Yang, S. Lin, J. Polym. Sci. A 38 (2000) 4258.

[91] (a) P.J.W. Deckers, B. Hessen, J.H. Teuben, Organometallics 21 (2002) 5122;
(b) P.J.W. Deckers, B. Hessen, J.H. Teuben, Angew. Chem. Int. Ed. 40 (2) (2001) 2516;
(c) P.J.W. Deckers, B. Hessen, WO 02/066404 (Stichting Dutch Polymer Institute), August 29, 2002;
(d) P.J.W. Deckers, B. Hessen, WO 02/066405 (Stichting Dutch Polymer Institute), August 29, 2002.

[92] J. Huang, T. Wu, Y. Qian, Chem. Commun. (2003) 2816.

[93] K. Sugimura, T.S. Nitabara, T. Fujita, JP 10324710 (Mitsui Chemicals Incorporated), December 8, 1998.

[94] K. Ban, T. Hayashi, Y. Suzuki, JP 11060627 (Mitsui Chemicals Incorporated), March 2, 1999.

[95] K. Ban, T. Hayashi, Y. Suzuki, JP 10101587 (Mitsui Chemicals Incorporated), April 21, 1998.

[96] (a) G.V.Z. Schulz, Phys. Chem., Abt. B 30 (1935) 379;
(b) G.V.Z. Schulz, Phys. Chem., Abt. B 43 (1939) 25;
(c) P.J. Flory, J. Am. Chem. Soc. 62 (1940) 1561.

[97] (a) P. Cossee, J. Catal. 3 (1964) 80;
(b) E.J. Arlman, P. Cossee, J. Catal. 3 (1964) 99.

[98] (a) J.X. McDermott, J.F. White, G.M Whitesides, J. Am. Chem. Soc. 95 (1973) 4451;
(b) J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.

[99] M.P. McDaniel, Adv. Catal. 33 (1985) 47.

[100] N. Meijboom, C.J. Schaverien, A.G. Orpen, Organometallics 9 (1990) 774.

[101] L.A. MacAdams, G.P. Buffone, C.D. Incarvito, J.A. Golen, A.L. Rheingold, K.H. Theopold, Chem. Commun. (2003) 1164.

[102] T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 1304.

[103] W.J. van Rensburg, C. Grově, J.P. Steynberg, K.B. Stark, J.J. Huyser, P.J. Steynberg, Organometallics 23 (2004) 1207.

[104] Z. Yu, K.N. Houk, Angew. Chem. Int. Ed. 42 (2003) 808.

[105] A.N.J. Blok, P.H.M. Budzelaar, A.W. Gal, Organometallics 22 (2003) 2564.

[106] T.J.M. de Bruin, L. Magna, P. Raybaud, H. Toulhoat, Organometallics 22 (2003) 3404.

[107] S. Tobisch, T. Ziegler, Organometallics 22 (2003) 5392.

[108] E.Y. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.

[109] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley, New York, 1999 p. 1355.