

Olefin Oligomerization via Metallacycles: Dimerization, Trimerization, Tetramerization, and Beyond

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1. INTRODUCTION AND SCOPE

The oligomerization of olefins (particularly ethylene) to higher oligomers continues to be an area of intense research activity, within both industry and academia. The main products of ethylene oligomerization, linear α -olefins (LAOs), are valuable building blocks for a range of industrial and consumer products, including comonomers, surfactants, and synthetic lubricants.^{1–3} The oligomerization of ethylene is predominately carried out using transition metal and aluminum catalysts that produce a geometric, or full-range, distribution of LAOs, such as

a Schulz–Flory distribution from Ni catalysts (SHOP) and a Poisson distribution from alkyl aluminum (alfene or ethyl process).^{1,2} These distributions result from a linear coordination-migratory insertion (Cossee) mechanism of chain growth (Scheme 1), and increasingly the full range of chain lengths does not match market demand.⁴ In particular, around one-half of the LAOs produced are employed as comonomers for the production of linear low-density polyethylene (LLDPE) copolymers, which utilize 1-butene, 1-hexene, and 1-octene fractions. Continually increasing demand for these short-chain oligomers has led to interest in more selective oligomerization technologies, in which the production of less valuable, or lower-volume LAOs, can be largely avoided. In this respect, the oligomerization of ethylene via metallacycle intermediates has proven to be extremely useful for selective 1-butene, 1-hexene, and 1-octene production.^{3,5,6}

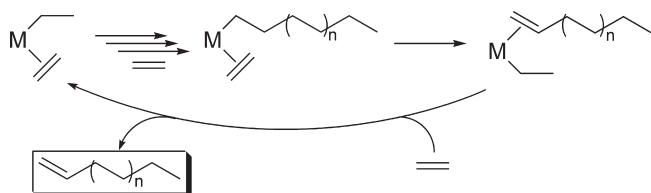
A generalized mechanism for this transformation is shown in Scheme 2. The process begins with oxidative (with respect to the metal) coupling of two ethylene units to produce a metallacyclopentane complex. From here, insertion of further ethylene into the metallacyclopentane produces larger ring metallacycles, while decomposition of the metallacycle at any point can produce linear α -olefins. The selectivity of the process is thus controlled by the relative stability of the different sized metallacycles, in particular their propensity to either decompose or grow via ethylene insertion. The aim of this review is to highlight recent advances in this area. The field of ethylene trimerization to 1-hexene was comprehensively reviewed by Morgan and co-workers in 2004.⁵ As such, this review will primarily focus on developments from 2004 onward. At the same time, reference to important older work will be made in order to provide a background (section 2). In addition, alkene dimerization, much of which predates 2004, will be covered because it was not included in Morgan's review. The cyclooligomerization of alkynes, diene oligomerization, and alkyne/alkene cooligomerization, which in many instances follow a metallacycle mechanism, have been extensively reviewed.^{7–10} As such, these processes will not be covered in the current review, despite the similarities between these reactions and alkene homooligomerization via metallacycles. The well-known metathesis method of olefin oligomerization and polymerization, which proceeds via carbene and metallacyclobutane intermediates, is also not covered herein.^{11,12} Although the bulk of the work revolves around ethylene oligomerization to short-chain LAOs (comonomers), the possibility

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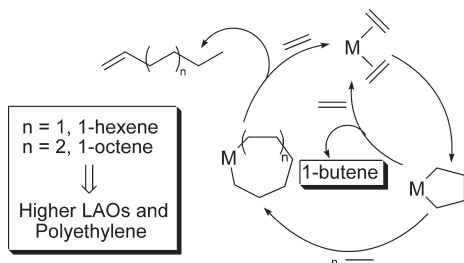
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Scheme 1



Scheme 2. Simplified Metallacycle Mechanism



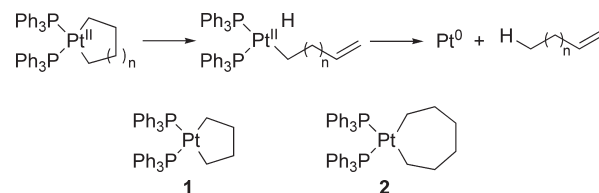
of large ring metallacycles leading to polyethylene formation is also of past and recent importance and will be covered as well. Throughout this review, catalyst activities are expressed as turnover frequencies (TOFs) of the monomer, usually ethylene $[(\text{mol of ethylene oligomerized}) \cdot (\text{mol of metal})^{-1} \cdot \text{h}^{-1}]$.

2. BACKGROUND

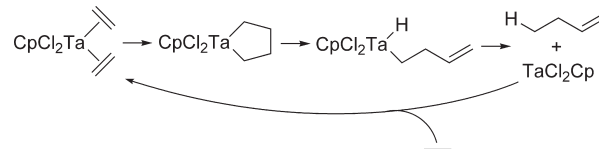
Metallacycles of the transition metals were well-known and extensively studied in the 1970s and 1980s^{8,13,14} and have been reviewed recently.^{15,16} Whitesides and co-workers prepared a range of platinum metallacycles and studied their decomposition,^{17,18} finding that the major product in each case was an α -olefin. The reaction was proposed to occur via stepwise β -hydride elimination to generate a metal hydride, followed by reductive elimination (Scheme 3). It was shown that the metallacyclopentane **1** decomposes much more slowly than large metallacycles, such as the metallacycloheptane **2**. This was thought to be due to the constrained geometry of the metallacyclopentane, which hinders or even prevents β -hydride elimination.¹⁹ Recent theoretical studies on titanium complexes support this proposal.^{20–22} Similar observations have been made with chromacyclopentanes and chromacycloheptanes.²³ The formation of metallacyclopentanes via oxidative addition of olefins was observed early on^{10,14,24–27} and ultimately paved the way for construction of a catalytic process. For instance, Schrock and co-workers found that tantalum complexes catalyze the dimerization of α -olefins via metallacycles (Scheme 4).^{28,29} Titanium complexes were likewise active.³⁰ These researchers were quick to realize the advantage of this approach to dimerization; because the metal hydride is short-lived, little or no isomerization of the α -olefin product occurs. The development of highly active titanium catalysts that are thought to operate via this mechanism paved the way for the selective large-scale production of 1-butene from ethylene (section 3).³¹

Around the same time, a metallacycle mechanism for the trimerization of ethylene to 1-hexene (section 4) was proposed by Union Carbide researchers,^{32,33} who can be credited with the discovery of this reaction.⁵ It is now known that trimerization can

Scheme 3



Scheme 4



come about when further olefin insertion (metallacycle growth) is more facile than elimination of 1-butene, according to Scheme 2. This is normally the case because of the stability of metallacyclopentanes, whereas the instability of metallacycloheptanes leads to selectivity to 1-hexene (as opposed to further metallacycle growth). More recently, however, it has been shown that the energetics of metallacycle growth and decomposition can be tuned such that selective tetramerization is possible (section 4).³⁴ As such, metallacycles have achieved a trifecta in terms of selective α -olefin production; all three of the highest-volume comonomers, 1-butene, 1-hexene, and 1-octene, can be made *selectively* through this route. Thus, from origins in fundamental chemistry, metallacyclic complexes have become extremely important catalyst intermediates in large-scale industrial chemistry. The industrial importance of ethylene dimerization is elaborated on in section 3, whereas ethylene trimerization was commercialized by Chevron Phillips in 2003.⁵ Additionally, IFP Energies nouvelles has recently started marketing a new chromium-based trimerization process.³⁵ Finally, at the time of writing, the Sasol ethylene tetramerization system (section 4) has entered basic engineering, with a view to commercialization.³⁶

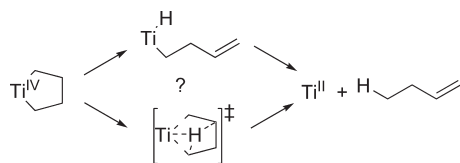
3. ETHYLENE DIMERIZATION

The dimerization of ethylene to 1-butene represents a great success for homogeneous catalysis in an industry dominated by heterogeneous processes. As discussed above, a variety of transition metal complexes catalyze this reaction through a metallacyclic mechanism. Modified Ziegler catalysts do so with high efficiency and were exploited to develop the Alphabutol process discussed below.

3.1. Alphabutol Process

The origins of this process lie with the discovery by Karl Ziegler and Heinz Martin that titanium and zirconium alkoxides, in combination with AlEt_3 , catalyze the conversion of ethylene to 1-butene with high selectivity.³⁷ Around 20 years later, Chauvin and co-workers at IFP exploited this chemistry to develop the so-called Alphabutol process for 1-butene production.^{3,31,38,39} The best catalyst system seems to be $\text{Ti}(\text{OBu})_4/\text{AlEt}_3$, which can achieve TOFs approaching $1 \times 10^6 \text{ h}^{-1}$. Zirconium alkoxides, while exhibiting similar selectivity, display a much lower activity.³¹

Scheme 5



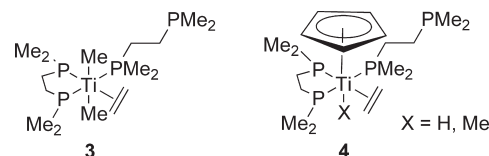
The optimal selectivity to 1-butene is $\sim 93\%$, with the only coproducts of note being branched hexenes that arise from 1-butene/ethylene codimerization. The formation of these is controlled by limiting ethylene conversion, which effectively keeps the ethylene concentration high enough to largely out-compete the codimerization reaction.

The generally accepted mechanism for this transformation is a Ti(II)/Ti(IV) metallacycle mechanism, although the structure of the active catalyst is not well-known.^{2,3,31,38} It is important to point out, however, that the mechanism of this catalyst is not nearly as certain as is sometimes portrayed in the literature. While there is evidence for the metallacyclic route,⁴⁰ it seems equally possible that other mechanisms are operative. For instance, the product output can be just as reasonably explained by a Cossee mechanism, in which a very high rate of chain transfer leads only to dimers. Early deuterium labeling studies support such a route, or alternatives.⁴¹ When a mixture of CH_2CH_2 and CD_2CD_2 was codimerized with an Alphabutol catalyst composition, H/D scrambling between the oligomers was observed. This observation is inconsistent with a metallacycle mechanism, in which no scrambling should be observed, and instead the isotopomer distribution observed is a very good match for that expected from a Cossee mechanism. Of relevance here are reports of highly selective dimerization of α -olefins with tungsten(VI)–imido complexes. Initial theoretical studies indicated that a metallacycle mechanism was feasible;^{42,43} however, more recent experimental work confirms a Cossee mechanism is most likely.⁴⁴ This result thus cautions that the observation of selective oligomerization, and lack of isomerization, does not necessarily equate to a metallacycle mechanism. As such, in the author's opinion, there are serious doubts over whether the Alphabutol system operates via metallacycles. Nonetheless, this seems to have become the leading proposal, and as such a discussion of this system is warranted herein.

If the metallacycle mechanism is operative, it is also uncertain whether 1-butene elimination occurs via a stepwise process (β -hydride elimination/reductive elimination) or a concerted 3,5-hydrogen shift (Scheme 5). Recent theoretical results suggest the stepwise process is easiest for metallacyclopentanes.^{20–22} As discussed above (section 2), this process is thought to be difficult due to the constrained geometry of the metallacyclopentane ring, and as such ethylene insertion and further metallacycle expansion is envisaged to be likely as a general rule. The Alphabutol process may thus be the exception that proves the rule. If so, it is quite the exception; there are currently 27 Alphabutol units operating worldwide with a total production capacity of 570 000 tons per annum, or 25% of the world's 1-butene supply.³

Studies by Girolami and co-workers on well-characterized single-site titanium complexes perhaps shed some light on how this process may be selective for dimerization.^{45,46} Complexes 3 and 4 have been characterized and react with excess ethylene to produce a similar product distribution to the Alphabutol catalyst. A metallacycle mechanism is likely, and it is particularly noteworthy that no insertion of ethylene into the Ti–H or Ti–Me

bonds of 3 and 4 occurs. Thus, ethylene insertion is clearly not favorable, which explains why metallacyclopentane expansion does not occur. As such, it is not necessary that metallacyclopentane decomposition to 1-butene be particularly facile, because in the absence of metallacycle expansion, selectivity to dimers may be the only course available.



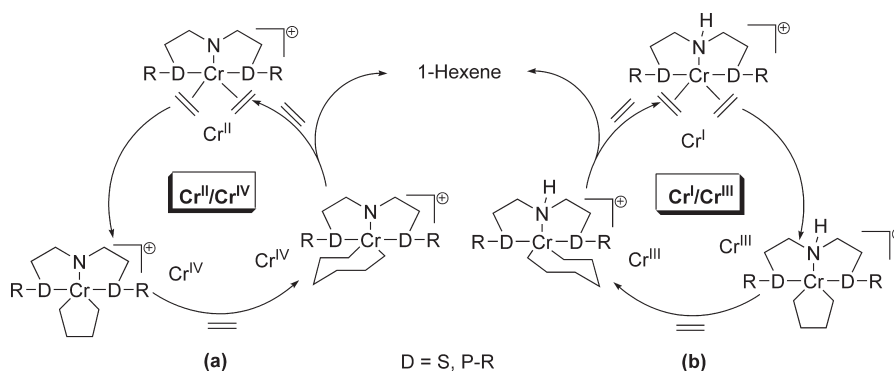
4. ETHYLENE TRIMERIZATION AND TETRAMERIZATION

4.1. Chromium Catalysts

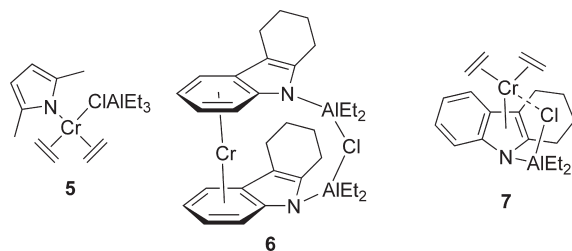
The first examples of catalysts selective for ethylene trimerization to 1-hexene were based upon chromium (section 2),⁵ and this metal still features in the vast majority of trimerization catalysts (and more recently tetramerization). Recent work has focused not only on development of improved catalysts but also on a mechanistic understanding of existing systems. This is confounded by the paramagnetic nature of the various chromium oxidation states, making NMR spectroscopy more challenging, and the possibility of different chromium spin states, which renders theoretical studies more difficult. Nonetheless, a number of theoretical investigations have appeared and support a metallacycle mechanism.^{47–49} Köhn has recently highlighted the potential difficulties facing theoretical chemists with these systems, by raising the possibility of spin state changes during the catalytic cycle.⁵⁰ Much experimental work has been carried out in order to ascertain the oxidation state of the Cr catalysts. It is important to point out, however, that one particular redox couple is unlikely to be responsible across the board. In the author's opinion, it is more likely that a number of chromium oxidation states are possible [Cr(I)/Cr(III), Cr(II)/Cr(IV), others?], dependent upon the supporting ligation on the catalyst. Oxidation state formalism says little about the actual electronic configuration at the chromium center. It may be that, after ligand effects are taken into account, the various chromium catalysts do have similar electron densities at the metal center. This possibility is not reflected when formal oxidation states are assigned. This new research on chromium systems, carried out since Morgan and co-workers' 2004 review, is detailed below, beginning with the commercial Phillips trimerization catalyst.

4.1.1. Phillips Trimerization System. The Phillips trimerization catalyst (not to be confused with the Phillips catalyst for ethylene polymerization, section 7) is thus far the only ethylene trimerization system to be commercialized. A detailed background to this catalyst was provided in Morgan and co-workers' work.⁵ The system is employed by Chevron–Phillips to produce ca. 47 000 tons per annum of 1-hexene. The catalyst is composed of a chromium source, 2,5-dimethylpyrrole, and an alkylating agent such as AlEt_3 and has been proposed to operate via a Cr(II)/Cr(IV) mechanism starting from a chromium complex such as 5.⁴⁷ The pyrrole ligand is thought to flip between η^1 and η^5 coordination throughout the catalytic cycle, effectively compensating for changes in the coordination environment at chromium. Recent reports from Gambarotta and co-workers provide good evidence for a Cr(I)/Cr(III) mechanism, however.^{51,52} By utilizing more bulky pyrrole ligands, single-site self-activating catalysts such as 6 could be isolated. This chromium(I) complex behaves similarly to the Phillips trimerization catalyst, and a catalytic cycle

Scheme 6



proceeding through an intermediate such as **7** was proposed, in which the chloro group acts in a hemilabile fashion. It is noteworthy that the proposed interaction between chromium and a chloro group is in general agreement with the known ability of chloro compounds to improve both activity and selectivity in this system.^{5,53} Furthermore, a recent electron paramagnetic resonance (EPR) study of the Phillips system also provides support for a Cr(I)/Cr(III) mechanism.⁵⁴ Armed with these experimental insights, Budzelaar has revisited the theoretical treatment of the Phillips system and found that such a Cr(I)/Cr(II) mechanism is quite feasible.⁵⁵ As such, the mechanistic details surrounding this catalyst remain uncertain, despite its importance to the field.



A recent patent describes what is perhaps best described as a “modified Phillips system”.⁵⁶ Herein, chromium and tantalum were immobilized on silica and activated with pyrrole, AlEt_3 , and an organochloro compound. It is unclear, however, which metal is responsible for trimerization, as tantalum is also known to promote this transformation (section 4.3). At any rate, the activities reported are rather low (up to ca. $9\,000\text{ h}^{-1}$), and the advantages of this over the homogeneous Phillips system are not obvious.

4.1.2. Bis(phosphino)amine and Bis(sulfanyl)amine Chromium Complexes [Ligand = $(\text{R}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$ and $(\text{RSCH}_2\text{CH}_2)_2\text{NH}$]. The well-known class of chromium catalysts based upon $(\text{R}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$ and $(\text{RSCH}_2\text{CH}_2)_2\text{NH}$ ligands were covered in Morgan and co-workers’ review,⁵ but a significant amount of further work has been carried out in order to understand the structure of the active catalysts. As such, a short background to these catalysts is required. McGuinness and Wasserscheid originally prepared precatalysts of structure **8**, which, upon activation with methylaluminoxane (MAO), formed highly selective catalysts for 1-hexene production.⁵⁷ Second-generation catalysts of structure **9** were later reported, which represented an improvement in terms of ease of ligand preparation and cost.⁵⁸ Optimization of catalysts **9** by researchers at Sasol Technology showed that they could be operated with very low levels of MAO (30–100 equiv) and that very high overall

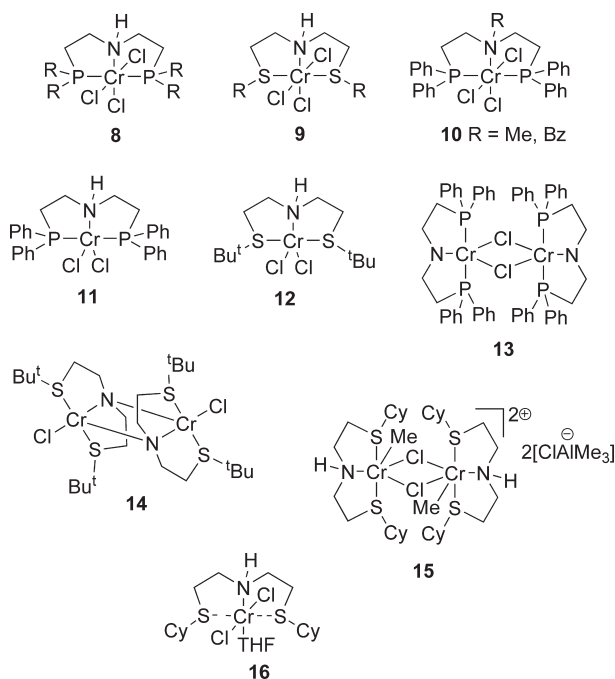
1-hexene selectivities ($>97\%$) were achievable. TOFs up to around $300\,000\text{ h}^{-1}$ were reported.

Recent studies on these systems have focused on elucidating the structure and oxidation state of the active catalyst, as well as the precise role of MAO. Precatalysts **8** and **9** contain N–H functionality, and there is interest in ascertaining whether or not this is preserved in the active species. Direct analogues of **8** containing N-alkyl functionality (**10**) were prepared and tested following activation with MAO.⁵⁹ These complexes displayed very low activity and 1-hexene selectivity, instead generating between 30 and 70% polyethylene. The authors concluded that N–H functionality is essential for high activity and selectivity with this ligand class. This led to speculation that the N–H group is deprotonated during activation, leading to a monoanionic tridentate ligand.

Follow-up studies concentrated again on the N–H functionality, as well as the Cr oxidation state and role of MAO.⁶⁰ Chromium(II) complexes **11** and **12** were prepared, and it was found that activities and selectivities to 1-hexene were broadly similar to the original Cr(III) complexes. This led to the conclusion that Cr(III) precursors are reduced to Cr(II) or lower upon activation with MAO, assuming that MAO is not able to oxidize Cr(II) back up to a higher oxidation state (it was subsequently found by other researchers that this is not always a safe assumption, below). Deprotonation of complex **11** with the organic base DABCO (1,4-diazabicyclo-(2.2.2)octane) led to the amido complex **13**, whereas reaction of $\text{LiN}(\text{CH}_2\text{CH}_2\text{S}^t\text{Bu})_2$ with $\text{CrCl}_2(\text{thf})_2$ led to complex **14**. Both dimer complexes feature N–H deprotonated ligands, and importantly, both were active catalysts for ethylene trimerization. The activity of **14** was greatly attenuated relative to monomeric precursors; however, the catalytic relevance of such a structure is uncertain. Its formation may result more from the absence of other ligating compounds (ethylene, MAO, AlMe_3), and under catalytic conditions, it may not form. Nonetheless, the fact that both deprotonated complexes, particularly **13**, were active for ethylene trimerization was taken as significant evidence that these ligands are deprotonated under the conditions of catalysis.

Independent but closely related studies of Gambarotta, Duchateau, and co-workers^{61,62} led to somewhat different conclusions on the issue of ligand deprotonation. When complex **9** with $\text{R} = \text{cyclohexyl}$ was reacted with AlMe_3 , the Cr(III) cationic dimer **15** was isolated.⁶¹ When MAO was used, an undefined complex was formed, thought also to be a Cr(III) cation of similar structure. When isobutylalumoxane was employed, instead a Cr(II) dimer was isolated (the same structure as **15** but without Cr–Me groups). In each case, the N–H group remains intact, and the authors suggested this as proof that deprotonation does not occur during catalysis.

A potential problem here, however, is that these model reactions are done at room temperature, whereas this class of catalysts are not active for trimerization under these conditions, requiring temperatures of 80–110 °C before good activity and selectivity result.^{57,58} Furthermore, the complexes are not effectively activated with the amounts of AlMe_3 or MAO utilized in these studies (ca. 5 equiv). It is thus difficult to draw concrete conclusions from studies that are not conducted under catalytically relevant conditions, particularly when elevated temperature and the amount of cocatalyst are so crucial to the operation of these catalysts. The authors also prepared an analogue of complex **14** with cyclohexyl substitution at sulfur and found this to be inactive in combination with MAO. This was interpreted as further evidence that the N–H group is not deprotonated, but here again, caution is required as the temperature of catalysis may be responsible for this observation. As discussed above, complexes **13** and **14** are in fact active at 80 °C, whereas the cyclohexyl analogue of **14** was tested at 50 °C. It was demonstrated in the original reports of these systems that, at 50 °C, the catalysts produce a high percentage of polymer and the activities are over 1 order of magnitude lower than at 80 °C.



Similarly to the work discussed above,⁶⁰ these authors also compared Cr(III) and Cr(II) precatalysts (including complex **16**) and again found that both oxidation states behave similarly once activated with MAO.⁶¹ This was again taken as evidence for reduction to Cr(II) or lower during catalysis. Later work by the same authors, however, raises some doubt over this.⁶² When the Cr(II) precursor $\text{CrCl}_2(\text{thf})_2$, SNS ligand, and 10 equiv of AlMe_3 were reacted, the Cr(III) dimer **15** was again isolated, along with Cr(0) resulting from a disproportionation reaction. This result clearly shows that the action of AlMe_3 on Cr(II) precursors can result in oxidation of the Cr center, and thus a Cr(III) active species remains a possibility.

The work of both research groups supports the notion of a cationic active species, as might be expected from MAO activation. McGuinness et al. showed that more well-defined perfluoroborane activators, known to generate cationic metal centers, are effective cocatalysts.⁶⁰ Gamborotta, Duchateau, and co-workers showed that reaction with alkyl aluminum reagents almost invariably

led to cationic complexes.^{61,62} Given this conclusion, two possible mechanistic cycles can be proposed (Scheme 6). That shown in Scheme 6a involves a Cr(II)/Cr(IV) redox couple and a mono-anionic ligand resulting from deprotonation. The alternative in Scheme 6b involves a Cr(I)/Cr(III) couple in which the ligand remains neutral. Of course, the possibility of hemilabile coordination of the S or P donors exists at each intermediate but is not shown in Scheme 6. It is clear that further work is required to definitively elucidate which of these mechanisms, or another, is operating. In this regard, theoretical analysis would no doubt be of benefit but is as yet lacking for this trimerization system.

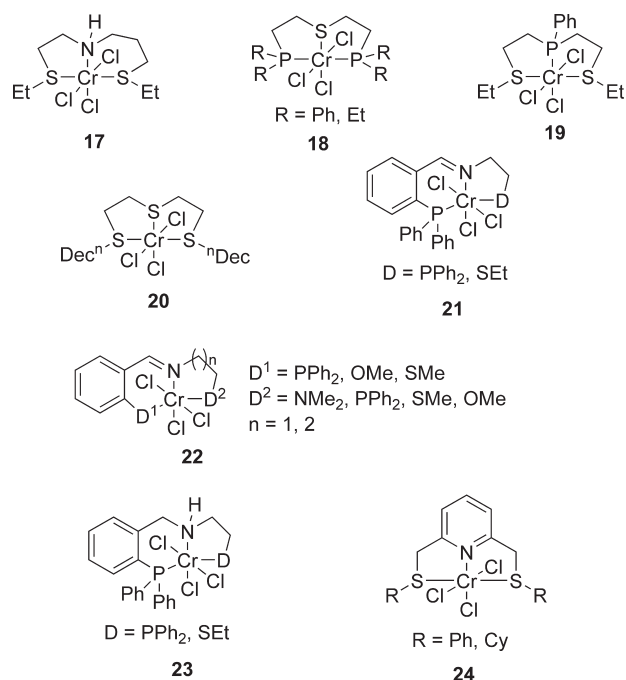
4.1.3. Chromium Complexes of Other Tridentate Ligands. The development of SNS–Cr catalysts spawned interest in alternative sulfur-based tridentates; however, thus far, none of these seem to have matched the original bis(sulfanyl)amine catalysts in terms of activity or selectivity. The effect of chelate ring size in these systems was explored through preparation of complex **17**, in which an extra methylene spacer group has been added to one side of the ligand.⁵⁹ Although this complex did give rise to an active trimerization catalyst (MAO activation), the productivity was around one-half that of the symmetrical analogue **9** and the selectivity to 1-hexene was lower. This result is in contrast to that for neutral tridentate PPP chromium catalysts,⁶³ in which such a change leads to a large increase in activity (with little change in selectivity).

The utility of S-donor-containing ligands was further explored by preparing a number of PSP and SPS chromium complexes, **18** and **19**.⁵⁹ Such complexes represent sulfur-containing analogues of PPP trimerization systems.⁶³ Complex **18** with Ph substitution led to a Schulz–Flory distribution of α -olefins once activated with MAO. With ethyl substitution, the major product was 1-hexene at low MAO loadings, which gave way to a C_6 -enriched Schulz–Flory distribution at higher MAO loadings. With both catalysts, the Schulz–Flory component of products had a K value of 0.51, which is similar to that obtained with unligated chromium.⁶⁴ The prospect of ligand abstraction from the chromium center seems possible, perhaps mediated by MAO or AlMe_3 . This was not realized at the time but was later postulated for similar SSS complexes (see below). The SPS complex **19** gave qualitatively similar results to those above, namely, a Schulz–Flory distribution of α -olefins ($K = 0.56$), which was enriched in C_6 . The TOFs of catalysts **18** and **19** ranged from 4 400–37 000 h^{-1} .

In later work, the SSS–chromium complex **20** was prepared and tested.⁶⁵ This produced around 70% 1-hexene with the remaining product being higher α -olefins. The TOF was 11 700 h^{-1} , although the catalyst was only active for a few minutes. Extended X-ray absorption fine structure (EXAFS) spectroscopic studies indicated that, upon treatment with AlMe_3 , significant dissociation from the chromium center occurs.

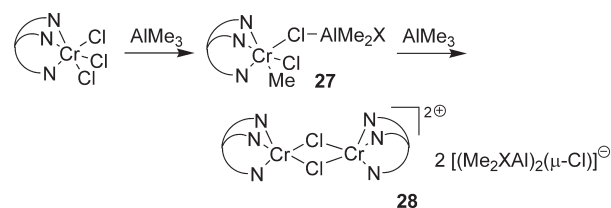
Bluhm and co-workers⁶⁶ tested a large range of tridentates with central imine or amine donors. The best catalysts from a trimerization perspective were those of structure **21**. When activated with MAO and run at 24–30 °C, ~82–86% 1-hexene was formed with the remainder being polyethylene (TOFs up to ca. 5 700 h^{-1}). Increasing the temperature seemed to shift the selectivity more toward polymer. A wide variety of other complexes, of general structure **22**, were also tested. Most of these gave mainly polyethylene (60+%), but the only other significant product in the majority of cases was 1-hexene, indicating high selectivity within the oligomeric products. Also tested were the amine complexes of structure **23**. These similarly produced 60–70% polyethylene, with the remainder being 1-hexene.

Somewhat related Cr–SNS complexes with a central pyridine donor, **24**, were later prepared and tested.⁶⁷ Activation with MAO produced catalysts with TOFs up to 9 800 h^{−1} and liquid product selectivities of 99% 1-hexene. The amount of polyethylene produced relative to 1-hexene was not explicitly given, but can be estimated as 5–22% from the data provided. A number of Cr(II) complexes of the ligand were also tested and found to produce more higher α -olefins at the expense of 1-hexene. The authors therefore suggested the possibility of a number of catalytic active species, Cr(II) leading to a Schulz–Flory distribution and Cr(III) generating 1-hexene. A Cr(I)/Cr(III) cycle analogous to that shown in Scheme 6b can be envisaged for these systems, along with the other neutral tridentate ligands discussed previously; however, this has hitherto not been studied (although it has been for Cr–triazacyclohexane catalysts; see below).

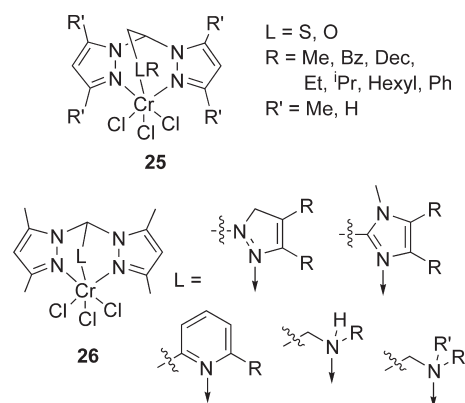


Whereas the tridentate ligands hitherto discussed display *mer* coordination (at least in the precatalysts), a number of systems are known that force a *fac* coordination geometry. Around a decade ago, the Tosoh Corporation developed catalysts based upon chromium in combination with the ubiquitous tris(pyrazolyl)methane ligands.⁵ These were discussed in Morgan and co-workers' review; however, in more recent, studies Hor and co-workers have investigated related heteroscorpionate systems.^{68–70} Complexes in which the third donor is oxygen or sulfur, of general structure **25**, were the first to be prepared and tested.⁶⁸ Both the thioether and ether complexes were selective for ethylene trimerization in combination with MAO. The ether analogues were superior, however, and the best catalyst (L = O, R = hexyl, R' = Me) led to an overall 1-hexene selectivity of 97.6% and a TOF of 39 000 h^{−1}. In recent follow-up studies, a broad range of complexes, **26**, were investigated in which the third donor group altered between pyrazolyl (Tosoh system), imidazolyl, pyridyl, and amine.^{69,70} All of these systems trimerize ethylene upon MAO activation. The complex with an imidazolyl moiety (R = H) was most active and selective (98 000 h^{−1}; 97.6% 1-hexene), whereas the amine group was the worst performer. In analogy to the work of Gambarotta with Cr–SNS complexes (above),

Scheme 7



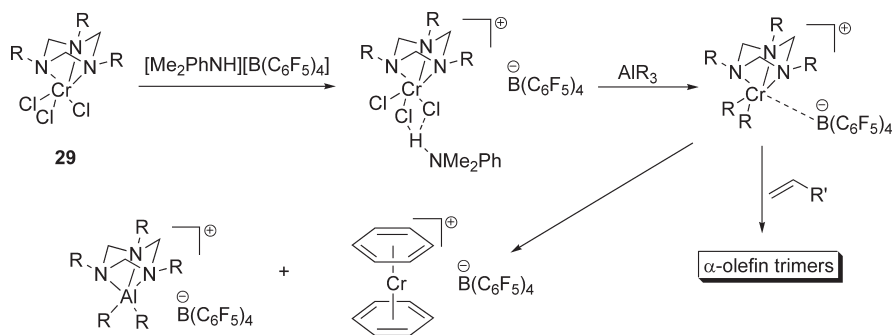
treatment of the tris(pyrazolyl)methane complex with AlMe₃ led ultimately to reduction to Cr(II) and cation generation (Scheme 7). The formation of the Cr(II) dimer, **28**, likely proceeded through the methyl–chromium(III) intermediate **27**. When activated with MAO, the Cr(II) species led to similar activity and selectivity to the Cr(III) precatalyst. A very recent report details similar NNN and NNO heteroscorpionate complexes of Cr(III) and Cr(II); however, these were found to lead to unselective (Schulz–Flory) oligomerization upon activation with MAO.⁷¹ The mechanism of this process was not investigated.



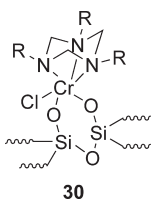
Köhn and co-workers developed chromium complexes of triazacyclohexane ligands and showed that these convert ethylene to mixtures of 1-hexene and polyethylene when activated with MAO or [Me₂PhNH][B(C₆F₅)₄]/AlⁱBu₃.^{5,72} When higher α -olefin monomers were used, the catalyst was highly selective for trimers, and mechanistic studies supported a Cr(I)/Cr(III) metallacycle mechanism.⁷³ These researchers have subsequently studied the activation process with [Me₂PhNH][B(C₆F₅)₄]/AlⁱBu₃ in more detail, and their observations provide insight into the likely mode of catalyst deactivation.⁷⁴ Treatment of the triazacyclohexane complex **29** with [Me₂PhNH][B(C₆F₅)₄]/AlⁱBu₃ first produces a more soluble anilinium adduct (Scheme 8). Treatment of this complex with triisobutylaluminum results in formation of a Cr(III) dialkyl cation. Reductive elimination from here is thought to produce a Cr(I) triazacyclohexane cation, which is active for α -olefin trimerization. However, reduction also leads to [(arene)₂Cr]⁺ and an aluminum–triazacyclohexane complex, which represent products of catalyst deactivation. The arene here is sourced from the solvent, and both the bis(benzene) and bis(toluene) complexes were characterized by X-ray crystallography.

Nenu and Weckhuysen⁷⁵ prepared silica-supported triazacyclohexane complexes of structure **30**, by treating the reduced Phillips polymerization catalyst⁷⁶ with triazacyclohexane ligands in dichloromethane. When this catalyst was activated with [Me₂PhNH][B(C₆F₅)₄]/AlⁱBu₃ and exposed to ethylene, a small amount of 1-hexene along with polyethylene was formed. Whereas the

Scheme 8



soluble products were 50–90% 1-hexene, the majority of product (>80%) was polyethylene. The authors claimed this system as a highly selective and highly active trimerization catalyst;^{75,77} however, this claim is not supported by the results presented. The activities presented are extremely low, with the maximum turnover frequency of 1-hexene below 10 h^{-1} . This contrasts with TOFs ranging from 10^4 – 10^6 h^{-1} (i.e., 4–6 orders of magnitude greater) for the more active systems reported in this review. Analysis of the polymer produced by this catalyst reveals some incorporation of 1-hexene (butyl branching), and as such, this work may be of some interest in the area of one-pot production of LLDPE if productivities can be increased (see section 6, Oligomerization–Polymerization Tandem Catalysis).



4.1.4. Diphosphinoamine Ligands—Ethylene Trimerization and the Discovery of Tetramerization. In 2002, researchers from BP reported on ethylene trimerization catalyzed by PNP ligands of structure **31**, in combination with a soluble chromium source and MAO.⁷⁸ The resultant catalysts were extremely active ($\text{TOF} > 1.8 \times 10^6 \text{ h}^{-1}$ at 20 bar) and showed relatively high selectivity to 1-hexene (ca. 80–90%). The major byproduct was reported to be C_{10} olefins derived from ethylene/1-hexene cotrimerization. The authors investigated a number of ligand combinations in which the *ortho*-methoxy substitution was replaced with *ortho*-ethyl or no substitution at this point, and concluded that this is vital for oligomerization activity. This was subsequently found not to be the case (below), although their theory that pendant coordination of the *ortho*-methoxy group occurs in this catalyst was proved to be correct. A full description of the BP trimerization system was provided in Morgan and co-workers' review,⁵ as well as in a mini-review by Wass.⁶

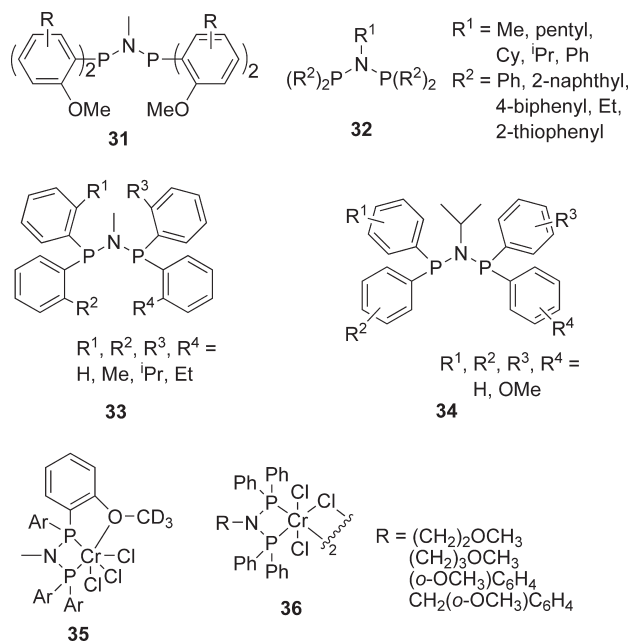
Modification of this ligand system by researchers from Sasol led to the discovery of selective tetramerization of ethylene to 1-octene.^{34,79} By removing *ortho*-substitution from the phenyl groups (structure **32**) and operating at elevated ethylene pressures, the first examples of catalysts selective for tetramerization were demonstrated. In this first report, 1-octene selectivity up to 70% was achieved, at TOFs up to $1.1 \times 10^6 \text{ h}^{-1}$. The other major products result from trimerization reactions, but not all of the C_6 fraction is made up of 1-hexene. Significant amounts (15–60%, ligand dependent) of methylcyclopentane and methylenecyclopentane

are also formed; their likely origin is discussed below. Polymer formation is generally quite low, <1%. Alternate phosphine substituents, other than phenyl, also gave rise to tetramerization catalysis. Thus, it was shown that bicyclic aromatic (2-naphthyl), heteroaromatic (2-thiophenyl), and alkyl (ethyl) phosphine substituents are also effective to varying degrees.

Follow-up work from Sasol has resulted in a reasonably good understanding of the factors that control the C_6/C_8 selectivity with these ligands. It turns out that steric interactions, brought about by *ortho*-substitution of the phenyl rings, are decisive in controlling the relative selectivity to trimerization or tetramerization. By testing a range of ligands of structure **33**, in which the size and number of *ortho*-substituents was varied, it was shown that the C_6/C_8 ratio is controlled by the overall steric bulk of the phosphines.⁸⁰ Thus, the C_6 selectivity ranged from >90% when 4 *ortho*-alkyl groups were present to <30% with only one *ortho*-methyl group present (>60% 1-octene). While this shows that pendant ether coordination is not a prerequisite for selective trimerization, it clearly favors formation of 1-hexene. This was demonstrated by testing ligands of structure **34** in which the position and number of methoxy substituents was varied.^{81,82} Only one *ortho*-methoxy substituent is required to shift the selectivity almost completely to trimerization. In contrast, *meta*- and *para*-methoxy substituents, in which intramolecular ether coordination is unlikely, behave more like unsubstituted ligands in terms of C_6/C_8 selectivity. The implication is that coordination of the *ortho*-ether group(s) is taking place, which was confirmed by Bercaw and co-workers, who isolated and structurally characterized a number of complexes such as **35**.⁸³ In addition, ^2H NMR studies revealed dynamic exchange of the ether groups in solution, suggesting that they could well exhibit hemilabile character during catalysis. A number of patents have also appeared recently in which *ortho*-F substituents are incorporated into the ligands.^{84,85} It is not clear, however, what effect these have on activity or selectivity; the results presented seem broadly consistent with published results in the absence of fluorine substitution.

It is now apparent that two separate, but no doubt related, effects mediate the switch from tetramerization to trimerization: ligand sterics and pendant donor coordination. It is not only donors on the phosphine aryl groups that can bring about this selectivity shift. The preparation and testing of complexes of structure **36**,⁸⁶ in which pendant ether donors are attached to the nitrogen backbone, led predominately to trimerization, although more tetramer results here than in catalysis with *ortho*-methoxy substitution on the phosphine aryl groups. Hor and co-workers also looked at related complexes containing thioether, ether, and pyridyl tethers on the nitrogen atom.⁸⁷ It is difficult to compare the selectivities reported herein with earlier studies, however, because catalysis was conducted at a rather high temperature (for these catalysts) of 80°C . A large

proportion of higher oligomers and polymer was formed, in addition to 1-hexene and 1-octene. Within the series tested, it is difficult to see any obvious trends with respect to the C_6/C_8 ratio versus the donor group. It has also been shown that intermolecular coordination of additional donors can lead to selectivity changes.⁸⁸ When the cocatalyst was changed from MAO to more well-defined cocatalysts (fluorinated aluminates and borates in combination with $AlEt_3$), it was found that the relative selectivity to 1-hexene and 1-octene obtained was strongly dependent upon the nature of the cocatalysts, in particular the coordinating ability of the anion. A range of selectivities from <5% C_8 (90% C_6) for more coordinating anions to 72% C_8 for extremely noncoordinating anions was observed.

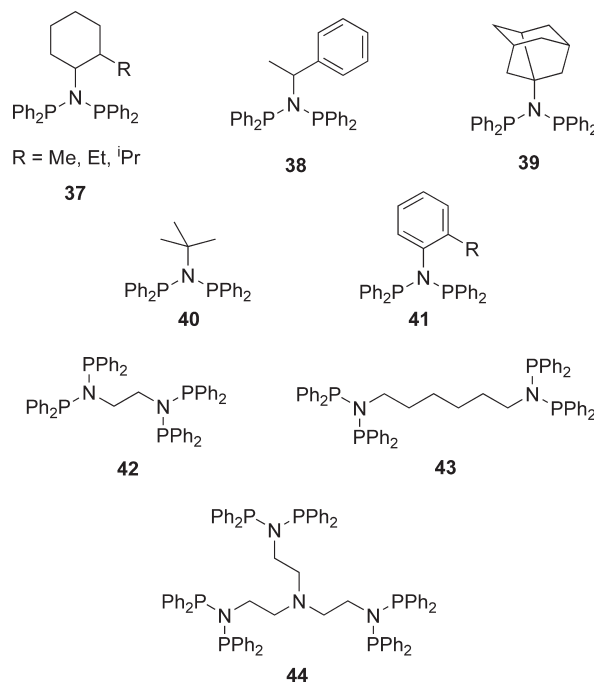


A large amount of work has been carried out in which the substituent, R, on the central nitrogen atom is altered in a broad range of ligands in the series $Ph_2PN(R)PPh_2$.^{89–93} Initial indications from the first report of ethylene tetramerization³⁴ were that, with cyclohexyl N-substitution, 1-hexene selectivity within the C_6 products was increased at the expense of undesirable methyl- and methylene cyclopentane, while 1-octene selectivity remained reasonably constant. Thus, a wide range of cycloalkyl-substituted ligands have been tested, from R = cyclopropyl through to R = cyclododecyl. Jiang and co-workers were the first to report cyclopropyl- and cyclopentyl-substituted ligands and suggested these lead to higher 1-octene selectivity (relative to R = i Pr).⁸⁹ In one run reported herein (cyclopentyl substitution), the C_8 fraction accounted for 89.8% of the products, with only 3.7% of C_6 products. A somewhat more systematic study was carried out by Wasserscheid and co-workers.⁹⁰ They found that an increase in ring size from cyclobutyl through to cyclododecyl led to an incremental improvement in combined 1-hexene and 1-octene selectivity (termed the total α -selectivity), mainly due to lower amounts of cyclic C_6 's. Catalyst activity also increased, probably due to increased catalyst solubility. The authors went on to study the effect of 2-substitution on N-cyclohexyl ligands, as in structure 37. Again, increased steric bulk on the nitrogen led to increased total α -selectivity. It was also noted that this increase in steric bulk shifted the selectivity toward trimerization at the expense of

tetramerization. The same group of authors conducted a further detailed study of N-substitution effects, in which a large range of branched-alkyl and -cycloalkyl substituents were tested.⁹¹ Although an in-depth analysis of every ligand permutation is probably unwarranted here, the conclusions of this study are worth noting. The dominant parameter influencing selectivity is the steric bulk of the N-substituent, with the basicity of this group being less important. Branching in the α -position is essential to maximizing the selectivity to 1-octene, for example, ligand 38. At the same time, a further increase in steric bulk, for instance, 39 and 40, leads to a selectivity shift toward 1-hexene. Optimization of ligands of this class led to exceptional productivities (TOFs up to 5.9×10^6 h^{-1}) along with very high total α -selectivity of ~88%.

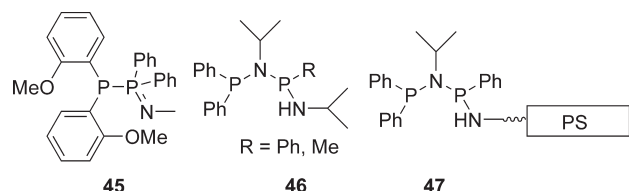
The influence of N-aryl functionality was also investigated by Killian et al.⁹² The findings here were not dissimilar to those described above. Again, the selectivity was mainly dependent upon the steric bulk attached to nitrogen, and less so on the group's basicity. *Ortho*-substitution, as in ligand 41, was found to be important in maximizing 1-hexene and 1-octene selectivity. Jiang and co-workers⁹³ also studied the effect of N-aryl substitution; however, their findings conflict somewhat with those of Killian's group. This work claimed that *ortho*-aryl substitution leads to higher amounts of cyclic C_6 products, although the effect was small. In contrast, Killian demonstrated a clear, and very substantial, trend of lower cyclic C_6 formation with increasing *ortho*-aryl steric bulk.

Other modifications to this ligand class include the preparation of tethered double- and triple-site ligands such as 42, 43, and 44.^{91,94,95} There seems to be no real advantage to this, seemingly ruling out bimetallic cooperative effects. Indeed, the best activity out of 42 and 43 was achieved with the longer alkyl bridge, suggesting behavior more like separated ligands.⁹⁴ An improved activity with low (100 equiv) loadings of MAO was claimed with ligand 44 (L/Cr = 1:3); however, this was not benchmarked against a simple mono-PNP ligand under the same conditions.



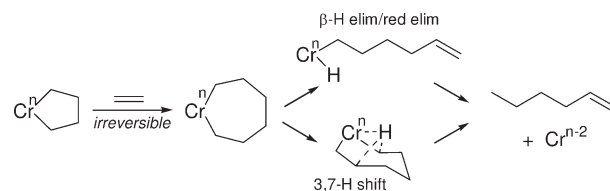
The patent literature details a number of somewhat unexpected modifications to these ligands. Shell researchers⁹⁶ prepared a number of iminodiphosphine ligands such as 45. Iminodiphosphines are

unstable isomers of the diphosphinoamines and are known to rearrange to the PNP structure upon coordination to some transition metals.⁹⁷ It was speculated in this patent that isomerization also occurs upon interaction with chromium, which seems reasonable given the results of catalytic testing. In combination with Cr/MAO, these compounds gave rise to active trimerization/tetramerization catalysts. However, there does not seem to be any obvious advantage to this approach. A number of patents have been filed in which a secondary amine is substituted on one phosphine, structure 46.^{98,99} These were used along with a chromium source and activated with AlEt₃. The best result was obtained when the chromium source was [(ⁱPr₂N)Cr(μ-ⁱPr₂N)]₂, perhaps suggesting the amido ligands or binuclear structure also play a role (binuclear structures have recently been suggested as possible intermediates; see below). Ethylene trimerization was observed when the second phosphine substituent was a phenyl group (TOF = 134 000 h⁻¹, 87% 1-hexene), which switched to tetramerization when this was a methyl group (19 400 h⁻¹, 82% 1-octene). A further patent and recent publication detail immobilization of this ligand to polystyrene beads through the amine, as shown in 47.^{100,101} Coordination of CrCl₃(thf)₃ and activation with AlEt₃ led to an anchored catalyst active for ethylene trimerization. The apparent activity is quite low (ca. 600 h⁻¹), although the system was claimed to be indefinitely active. A 40 h run was demonstrated. It was noted that immobilization led to increased polymer formation (9%) relative to the homogeneous system.¹⁰¹ These researchers have very recently published some of this work in the open literature.^{102–104} This work reveals that N–H deprotonation of the ligand is likely upon activation with AlEt₃. Such a P–N binding mode to chromium has been demonstrated,¹⁰⁵ while rearrangement to an inactive NPPN ligand structure has also been observed at elevated temperature.¹⁰⁶ The catalyst is considered by the authors to be a likely candidate for large-scale trimerization, due to the high purity of 1-hexene produced and the long catalyst lifetime. It is notable that very low amounts of cocatalyst are required (ca. 15 equiv of AlEt₃). Kinetic studies revealed a first-order dependence on both ethylene and catalyst concentration,¹⁰³ with an activation energy for 1-hexene formation of ~38 kJ·mol⁻¹.¹⁰⁷



These reports of activation with AlEt₃ are also relevant in the context of eliminating the need for MAO from the PNP tri/tetramerization system. The use of MAO, which is derived from relatively expensive AlMe₃, has economic implications when it comes to the large-scale use of this technology. The use of less-expensive activators (Al{(CH₂CH₂)_nEt}₃ or derivatives), or stoichiometric cocatalysts (noncoordinating anions) is therefore of interest. Unfortunately, using ethylaluminumoxane (EAO), which is prepared from inexpensive AlEt₃, is much less effective than using MAO.^{108,109} Together with a much lower activity, a large amount of 1-butene is coproduced along with 1-hexene and 1-octene. Isobutylaluminumoxane (ⁱBAO) performed likewise. Some investigations⁶⁴ have been carried out with the boranes/borates B(C₆F₅)₃ and [Ph₃C][B(C₆F₅)₄], which are well-known stoichiometric (alkyl-abstracting) activators used in ethylene polymerization.¹¹⁰ In combination with alkylating agents (AlEt₃, AlⁱBu₃), these cocatalysts did produce active catalysts; however, rapid deactivation

Scheme 9



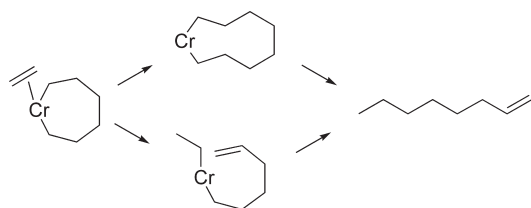
ensued and product selectivities suffered. It was subsequently shown that deactivation occurs through exchange between the borate anion and AlEt₃, leading to mixed ethyl–aryl borates and aluminates, such as [(C₆F₅)AlEt₃]⁻.⁸⁸ Such anions are expected to be much more coordinating than the perfluoro parents, and this was suggested as the reason for deactivation. As a result, a range of noncoordinating perfluoro aluminates were prepared and tested as cocatalysts, and it was shown that the effectiveness of the activator was related to the stability of the anion toward AlEt₃. The most effective cocatalyst was [Ph₃C][Al{OC(CF₃)₃}]₄, which contains an extremely stable and noncoordinating anion.¹¹¹ Together with AlEt₃ (Cr/aluminate/AlEt₃ = 1:1.5:100), this system led to a TOF of 230 000 h⁻¹ with very similar product selectivity to MAO activation.¹¹² Interestingly, it was also found that an excess of the trityl cation led to PNP ligand abstraction from the Cr center, which in turn leads to unselective oligomerization to linear α-olefins.⁶⁴

Previous work has shown that organo–chloro additives can have a beneficial effect on the Phillips trimerization system (section 4.1.1).⁵ Jiang and co-workers have therefore investigated the effect of a range of organochlorides on ethylene tetramerization with the Cr/PPN system.^{108,113} Increasing amounts of the chlorides led to modest increases in the 1-octene selectivity. At the same time, however, a marked decrease in activity occurs, and the effect of these additives cannot be considered beneficial. The mode of action of these compounds was not investigated.

A variety of mechanistic studies have been carried out with these catalysts. Bercaw and co-workers first investigated the system with *ortho*-methoxy aryl substitution (the trimerization selective catalyst).^{5,114} Deuterium labeling studies (CH₂CH₂/CD₂CD₂ copolymerization) strongly indicate a metallacycle mechanism for 1-hexene formation and rule out a conventional Cossee mechanism. This can be deduced from the lack of H/D scrambling within the product, which is consistent with a metallacyclic mechanism. Further deuterium labeling studies revealed that metallacycloheptane formation is irreversible but could not determine whether a concerted 3,7-H shift, or a stepwise β-hydrogen transfer followed by reductive elimination, leads to 1-hexene formation (Scheme 9).¹¹⁵ If a stepwise process is responsible, then the final reductive elimination must be fast relative to other possible reactions (such as reinsertion of the pendant alkene), as no isomerization or chain walking is observed (although this probably does occur with tetramerization ligands, as discussed later).

Researchers from Sasol¹¹⁶ subsequently studied ethylene tetramerization using similar methods to those introduced by Bercaw and co-workers. Deuterium labeling again indicated a metallacycle mechanism for 1-hexene and 1-octene formation, but H/D scrambling within the C₆ cyclics indicates a more complicated process for the formation of these. The route to 1-octene formation from the metallacycloheptane precursor, through either of the processes shown in Scheme 10, was considered. Analysis of the cotrimers and cotetramers of ethylene/1-hexene/1-octene shows that the Cr–ethyl route (bottom) is very unlikely to be operating. A number

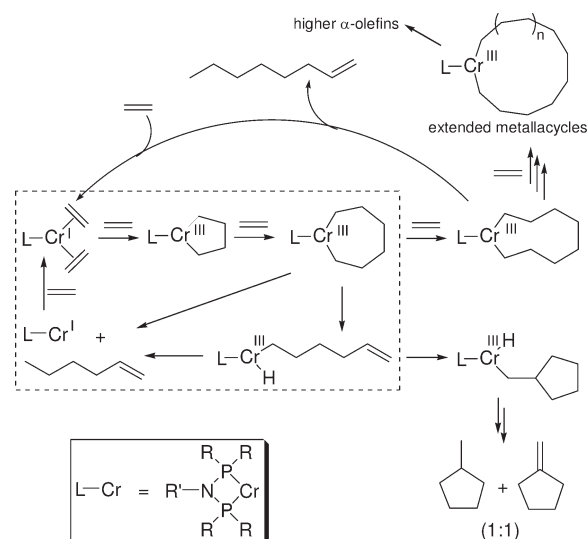
Scheme 10



of routes to methylcyclopentane and methylenecyclopentane were also considered, and the most likely was thought to be a bimetallic disproportionation reaction originating from the Cr–hexenyl hydride species, which is formed by β -hydride elimination.

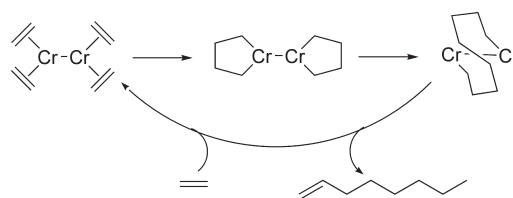
A mechanism that incorporates all products formed with these catalysts (with the exception of cotrimers and -tetramers) is shown in Scheme 11, and results from these and other mechanistic studies. With bulky PNP ligands, or pendant ether coordination, the process is restricted for the most part to those steps within the boxed section of Scheme 11, i.e., selective ethylene trimerization. With less bulky PNP ligands, a range of further processes become possible, which include ring expansion to chromacyclononane and larger metallacycles as well as reinsertion of the olefinic group of the Cr–hexenyl hydride. The absence of cyclic products with trimerization-specific ligands may indicate that 1-hexene formation only occurs through a concerted 3,7-H shift in these instances, whereas both routes to 1-hexene liberation are possible with ligands that allow tetramerization.¹¹⁵ Overett and co-workers showed that ethylene tetramerization catalysts also produce low levels of higher α -olefins (C_{10} – C_{20}) and that these come from an extended metallacycle mechanism. The chromacyclononane structure is the least stable of the large metallacycles, which explains the selectivity to 1-octene.¹¹⁶ An alternate possibility for 1-octene formation has very recently been proposed by Rosenthal and co-workers.¹¹⁷ They speculate on the involvement of binuclear intermediates in the formation of 1-octene (Scheme 12), on account of disphosphinoamine type ligands favoring a bridging coordination mode. There is, as yet, no direct experimental evidence for this proposal, and further investigations are necessary.

A range of studies, both experimental^{64,88,115,118–121} and theoretical,¹²² show that cocatalysts that are effective in this reaction lead to a dissociated ion pair (cationic chromium). As such, each intermediate in Scheme 11 is formally a cation, with the corresponding anion (normally MAO derived) omitted for clarity. Most of these studies also provide reasonable good evidence for a Cr(I)/Cr(III) mechanistic cycle as shown. Bercaw and co-workers showed that neutral triaryl PNP chromium complexes, which are initially inactive, give rise to ethylene trimerization upon cation generation and reductive elimination to Cr(I) (Scheme 13).^{115,118} A number of research groups prepared Cr(0) and Cr(I) carbonyl complexes with PNP ligands (Scheme 14).^{119,120} Neutral Cr(0) complexes were invariably inactive, while specific Cr(I) cationic complexes showed trimerization and tetramerization activity. Both groups found that abstraction of all CO ligands was necessary, and the only reagent found to accomplish this was $AlEt_3$. Noncoordinating counteranions were also essential, with BF_4 and PF_6 anions seemingly poisoning the catalysts. The best result was achieved with the noncoordinating and robust anion $Al\{OC(CF_3)_3\}_4$, which led to a TOF of $257\,000\ h^{-1}$.¹¹⁹ Another study of the system, which utilized in situ EPR spectroscopy, concluded that both $Cr(acac)_3/$

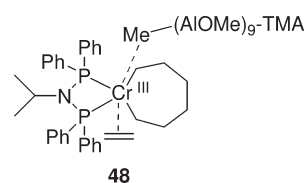
Scheme 11^a

^a Chromium complexes are cationic, with the charge and counteranion omitted for clarity.

Scheme 12

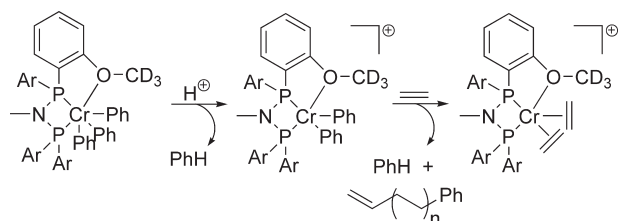


PNP and the preformed complex $[(PNP)CrCl_2(\mu-Cl)]_2$ are reduced to cationic Cr(I) upon treatment with MAO.¹²¹ The only theoretical study of this system to date considered the interaction of realistic MAO anion models with the proposed chromacycloheptane intermediate **48**.¹²² Again, a dissociated ion pair complex was found to be likely when large-cage MAO structures were modeled. One investigation has found that treatment of $[(PNP)CrCl_2(\mu-Cl)]_2$ with $AlMe_3$ leads to a Cr(II) cation.¹²³ This complex is not active for oligomerization, however, unless treated with excess MAO in the same manner as other precatalysts, and as such, its relevance to the catalytic cycle is uncertain.

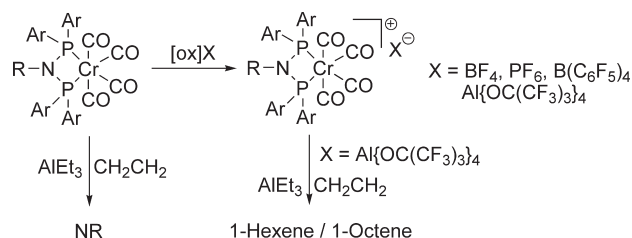


A number of kinetic investigations have been carried out with this system and are generally consistent with the above mechanistic proposal, although some observations require further explanation. Overall product formation was found to have an order in ethylene of 1.6 ($rate_{olig} \propto [ethylene]^{1.6}$).¹²⁴ It was suggested that this may indicate two competing reaction pathways with first- and second-order ethylene dependencies. More recent kinetic studies

Scheme 13



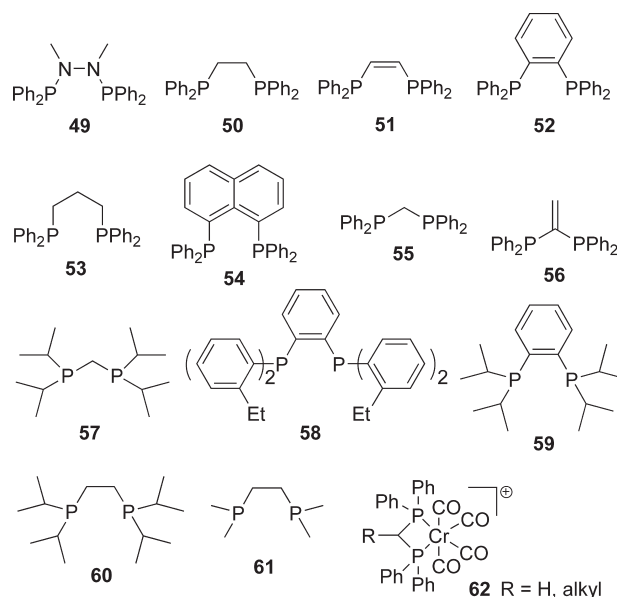
Scheme 14



seem to confirm this, whereby an overall order in ethylene of 1.67 was found to be composed of order in ethylene of 2.05 for 1-octene formation and 1.29 for 1-hexene formation.¹²⁵ Further investigation is therefore required to fully explain these findings. Increasing ethylene pressure leads to more 1-octene at the expense of 1-hexene, although the effect is modest, whereas the formation of C₆ cyclics is independent of pressure.¹²⁶ Product formation is first-order in chromium¹²⁴, and substoichiometric amounts of ligand with respect to chromium lead to loss of activity (and a shift to Schulz–Flory behavior).¹²⁷ This behavior, and the formation of odd-numbered olefins under substoichiometric conditions, has been attributed to the formation of ligand-free active species and chain transfer with AlMe₃.¹²⁸ The formation of C₁₀–C₁₄ products is primarily related to 1-hexene/1-octene/ethylene cotrimerization and cotetramerization and is dependent upon the concentrations of 1-hexene and 1-octene. As such, the amount of these undesirable side products formed is controlled by the time on stream (ethylene conversion).¹²⁴ Optimization during some of these kinetic studies led to very high activities and selectivities. For instance, a TOF of $6.8 \times 10^6 \text{ h}^{-1}$ along with 90% combined selectivity to 1-hexene and 1-octene was achieved in one study.¹²⁵

4.1.5. Other Chromium–Diphosphine Catalysts. Following the discovery of ethylene trimerization and tetramerization with diphosphinoamine ligands, it was perhaps not surprising to find that a range of other simple bidentate diphosphines are effective in combination with chromium. In the first report of tetramerization, it was found that the PNNP ligand **49** and the simple and ubiquitous dppe ligand, **50**, form tetramerization catalysts along with a chromium source.³⁴ Another PNNP ligand leads to mixed results.¹²⁹ Researchers from Sasol have since surveyed a range of carbon-bridged diphosphine ligands, **50**–**61**.¹³⁰ The ligand that is perhaps closest to diphosphinoamine ligands in terms of bite angle and sterics is dppe, **55**. Surprisingly, this ligand is ineffective for tri/tetramerization, instead giving a Schulz–Flory distribution of oligomers. It has been reasoned that this may be due to the acidity of the methylene protons on the ligand backbone, resulting in a noninnocent ligand. Ligand **57**, which should have less

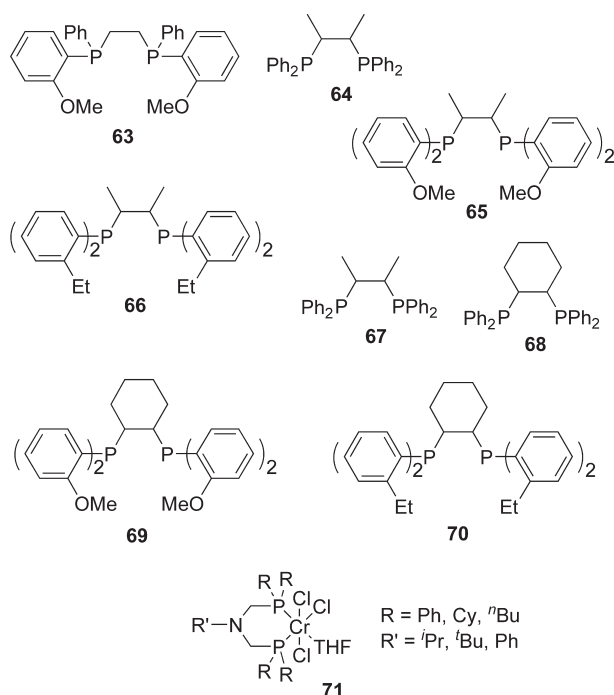
acidic methylene protons, was in fact found to be active for tetramerization. More recent work casts some doubt over this theory, however. Wass and co-workers prepared a range of Cr(0) and Cr(I) complexes such as **62** and found that the ligands, including dppe, were remarkably resistant to deprotonation.¹³¹ The backbone alkyl-substituted ligands did yield improved results over dppe, although they were still inferior to diphosphinoamine ligands. As such, the precise reason why diphosphines with a single carbon bridge are less effective remains unclear but most likely relates to steric and electronic factors.



The remaining ligands containing longer carbon bridges (**51**–**54**, **58**–**61**) were all found to produce active catalysts.¹³⁰ There seemed to be a general correlation between the P–Cr–P bite angle and the C₈/C₆ ratio, with small bite angles giving rise to the highest tetramerization selectivity. Modification of the P-substituents normally affects selectivity in the same fashion as for PNP catalysts (above), wherein bulky phosphines (e.g., *ortho*-phenyl substitution) lead to trimerization. At the same time, it was shown that phosphine electronics can also affect selectivity. A chromium complex of ligand **52** led to an exceptionally active catalyst (TOF > $13 \times 10^6 \text{ h}^{-1}$), which was also stable at high temperature, although selectivity to 1-octene was lower than with PNP ligands.

A wider range of ethylene-bridged diphosphines have been disclosed in the patent literature. A Shell patent¹³² shows that *ortho*-methoxy phenyl substitution, as in ligand **63**, leads to trimerization as was found for diphosphinoamine ligands. Oddly, another patent from SK Energy seems to show that incorporation of four *ortho*-methoxy phenyl substituents does not lead to an active catalyst.¹³³ The main scope of the SK Energy patents was dppe-type ligands incorporating alkyl substitution on the backbone, for example, **64**–**70**.^{133,134} This leads to *S,S*-, *R,R*-, and *meso*-stereoisomers, and all were tested. Whereas the *S,S*- and *R,R*- ligands were for the most part effective tri/tetramerization catalysts along with chromium and MAO, all of the *meso*-ligands led only to polyethylene. The most effective ligands were those containing a cyclohexyl backbone, **68**–**70**. With simple phenyl substitution, the selectivity to 1-octene was ~60–70%, while *ortho*-substituents (**69**, **70**) led to a switch to trimerization (80–90% 1-C₆). Unexpectedly, the *ortho*-substituted ligands

without a cyclohexyl backbone (**65**, **66**) were ineffective, leading only to polymer. As for diphosphinoamine ligands, it seems that subtle ligand influences have a pronounced affect on product selectivity.

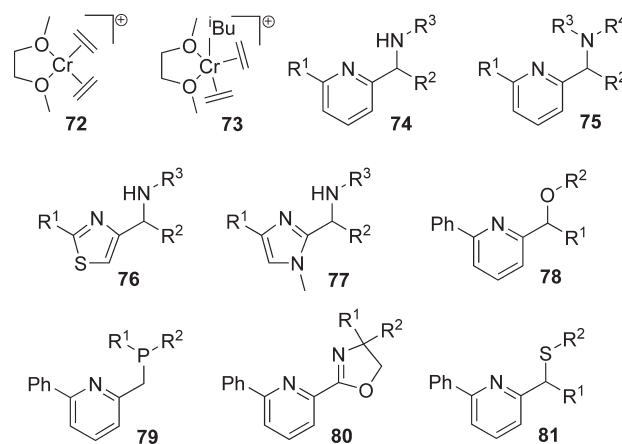


Yet another diphosphine motif was explored by Le Floch and co-workers, who prepared complexes of the form **71**.¹³⁵ Crystallography revealed a bidentate coordination mode, and after activation with MAO, the complexes catalyzed ethylene trimerization and, in a number of instances, tetramerization (up to ca. 20% 1-octene). With bulky cyclohexyl substitution of the phosphines, the catalysts were highly selective for 1-hexene (up to 97% overall, TOF ca. $18\,000\text{ h}^{-1}$). Theoretical methods were used to study metallacycloheptane decomposition to 1-hexene or expansion to chromacyclononane, assuming a Cr(I)/Cr(III) cationic mechanism. Liberation of 1-hexene was in all cases predicted to occur via a concerted 3,7-hydride shift, strongly assisted by chromium. It was also shown that steric bulk at the phosphines disfavors chromacyclononane formation, hence the experimentally observed selectivity to 1-hexene in these cases.

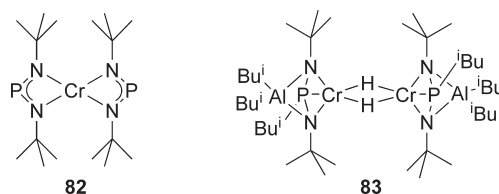
4.1.6. Chromium Complexes of Mixed Donor (O, N, S, P) Bidentates. The first truly selective ethylene trimerization system was a combination of chromium tris(3-ethylhexanoate), isobutylaluminum, and the bidentate ligand 1,2-dimethoxyethane, reported by Union Carbide in 1989.³³ It is only very recently that this system has been revisited, this time through the use of theoretical chemistry.¹³⁶ A range of models for possible intermediates were considered, and it seems that mechanisms starting from either the Cr(I) cation **72** or the Cr(II) cation **73** are most likely. As discussed in the preceding section, a concerted 3,7-H shift was found to be the lowest-energy pathway to 1-hexene liberation.

A large range of N,N-, N,O-, N,P-, and N,S-bidentates have been disclosed in a series of patents from Exxon-Mobil. High-throughput screening of ligands of general structure **74** and **75**,¹³⁷ **76** and **77**,¹³⁸ **78**,¹³⁹ **79**,¹⁴⁰ **80**,¹⁴¹ and **81**,¹⁴² in combination with various chromium sources and MAO, led to mixed

results for ethylene trimerization and tetramerization. The α -olefin selectivities presented in these patents are somewhat misleading, as polyethylene formation is not factored into these numbers. In some cases, for instance, 1-hexene selectivity is reported as 98+%, while well over 50% of the formed product constitutes polyethylene. The most active catalysts are formed when ligands **74** and **75** are employed (TOFs up to ca. $1.8 \times 10^6\text{ h}^{-1}$), and there is no doubt in this case that the catalysts are truly selective toward 1-hexene (up to ca. 98% 1-hexene inclusive of polymer). Ligands of structure **76** and **77** produced 1-hexene and 1-octene (up to ca. 50% 1-octene) but displayed a much lower activity. The results with the remaining ligands **78**–**81** seemed much less impressive. 1-Hexene is formed with very low activities (<500 turnovers), and the product is in most cases mainly polyethylene.



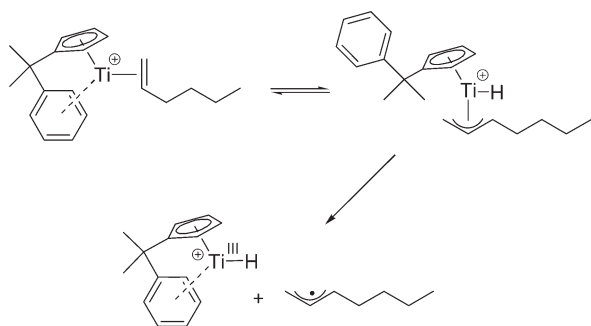
Gambarotta and co-workers have prepared Cr(II) complexes of NPN monoanionic ligands (structure **82**) and found these to be selective ethylene trimerization catalysts after activation with excess Al^iBu_3 .^{143–145} TOFs up to $\sim 21\,000\text{ h}^{-1}$ were achieved. Addition of MAO led to unselective oligomerization and polymerization. It was shown that the ligand in **82** is not innocent and that alkylaluminum reagents result in alkylation of the phosphorus atom and aluminum coordination. One of the intermediates that was isolated and that shows the (possibly) final ligand assembly is **83**, which resulted when **82** was treated with 10 equiv of Al^iBu_3 . The final identity of the active catalyst remains unclear, however; further addition of excess Al^iBu_3 is required before **83** becomes selective for trimerization.



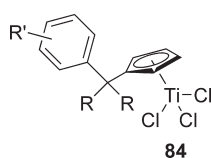
4.2. Titanium, Zirconium, and Hafnium (Group 4) Catalysts

Of the ethylene trimerization systems that are not chromium-based, those which stand out as some of the most active are the arene-substituted cyclopentadienyl titanium catalysts developed by Hessen and co-workers, of general structure **84**.^{5,146,147} These catalysts are capable of TOFs $\sim 240\,000\text{ h}^{-1}$ and produce up to 90% 1-hexene. The major secondary products formed are C_{10} 's, resulting from 1-hexene/ethylene cotrimerization (ca. 5–10%),

Scheme 15



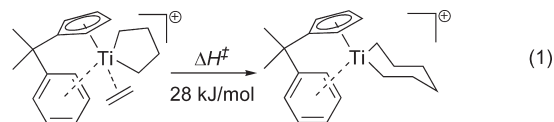
followed by polyethylene (ca. 1–2%). These catalysts were reviewed by Hessen in 2004.¹⁴⁸



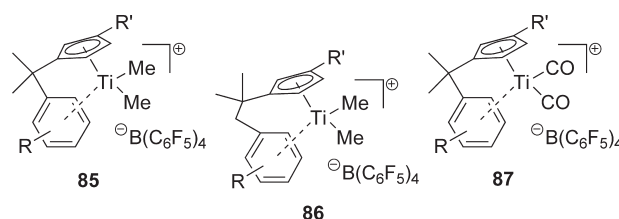
Recent experimental work has focused on kinetic studies and optimization of the reaction. Hagen et al.¹⁴⁹ have investigated factors affecting concomitant polymer formation, which is an important consideration when scale-up is contemplated. What, on paper, appear to be rather trivial levels of polymer formation (1–2%) rapidly become significant on a large scale. Quite apart from the obvious loss of efficiency in monomer, polymer formation can lead to reactor fouling, particularly with catalysts operating at low temperatures. It is probable that much research on high-activity trimerization and tetramerization systems has been directed toward understanding and reducing polymer formation, although most of this would have taken place within industry and has not been published. Hagen's work is one of the few systematic studies to be published in this regard. This work found that, when catalysts of structure **84** are activated with MAO, polyethylene formation results from two different species/processes. Early in the reaction (activation phase), rapid polymer formation ensues and is due to a partially alkylated titanium complex, $[\text{Cp}'\text{Ti}(\text{CMe})]^+$, which is an active polymerization catalyst. It was shown that alkylation of **84** with AlMe_3 does not instantaneously lead to the trimethyl complex. The polymer formation associated with this phase of catalysis can be largely avoided by a preactivation step (treatment of **84** with AlMe_3) or by starting with a preformed trimethyl precatalyst, $\text{Cp}'\text{TiMe}_3$. Over the length of the whole run, another phase of slow, continuous polymer formation takes place and is thought to be due to a degraded catalyst species. Polyethylene formation via this process is therefore an inherent property of the system. The authors demonstrated one degradation process leading to a $\text{Ti}(\text{III})$ –hydride and postulated this may lead to polymerization (Scheme 15).

In another study,¹⁵⁰ Hagen went on to study the kinetics of trimerization with this catalytic system. It was found that 1-hexene formation is first-order in ethylene concentration, which is consistent with a rate-determining step of ethylene insertion into a titanacyclopentane (Reaction 1). This finding is in accord with theoretical studies (below). The calculated enthalpy of activation for this step, ΔH^\ddagger , was $28 \text{ kJ}\cdot\text{mol}^{-1}$ ($\Delta S^\ddagger = -117 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), again in reasonable agreement with theoretical values. Catalyst deactivation was found to be second-order in the

concentration of titanium, indicating that this step involves an unidentified dimeric species. The activation enthalpy for this process was determined to be $76 \text{ kJ}\cdot\text{mol}^{-1}$.

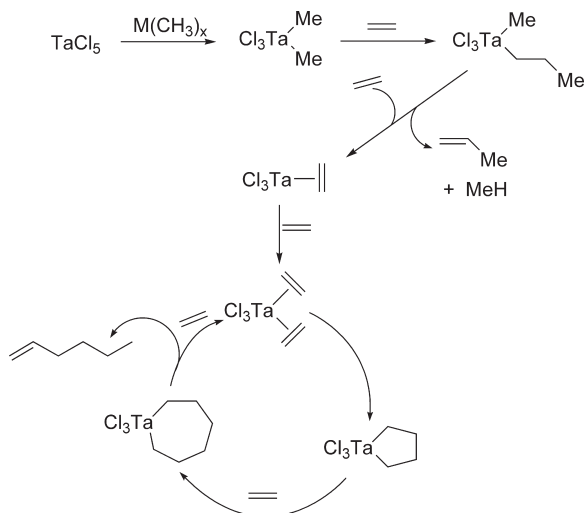


The initial reports of these catalysts led to a series of independent theoretical modeling studies from a number of groups.^{20–22} Although these were covered in Morgan and co-workers' review, a recap of the conclusions is warranted here. Activation with MAO leads to a $\text{Ti}(\text{II})$ cation through a sequence of alkylation, insertion, and reductive β -hydride transfer. From here, a $\text{Ti}(\text{II})/\text{Ti}(\text{IV})$ metallacycle mechanism is predicted to operate. The key to success with these catalysts seems to be the ability of the pendant arene group to act as a hemilabile ligand through ring-slippage. As metallacycle formation, growth, and decomposition occur, the arene group is able to moderate its coordination strength to suit changes in the metal center's sterics and electronics. At various points in the mechanistic cycle, the arene group shuttles between approximately η^1 -, η^3 -, and η^6 -coordination. Recent experimental work illustrates this, whereby the coordination behavior of the arene moiety was studied in complexes that model the proposed intermediates in the catalytic cycle.¹⁵¹ A number of crystal structures of complexes **85** and **86** were obtained, in which arene coordination is displayed. In complexes of structure **85** with a CMe_2 bridge, η^3 -like arene coordination character is observed, whereas the coordination is more consistent with η^6 -arene binding when a CMe_2CH_2 bridge is present, **86**. Variable-temperature NMR studies reveal hemilability in complexes of structure **85**, whereas in **86** they indicate tight arene binding. Consistent with this, CMe_2 -bridged complexes are active for ethylene trimerization, while CMe_2CH_2 -bridged complexes are not. The arene bonding in a $\text{Ti}(\text{II})$ species was represented by isolation of complexes of structure **87**, in which the arene is no longer noticeably hemilabile. In this work, these bonding interactions were also studied by theoretical calculations.

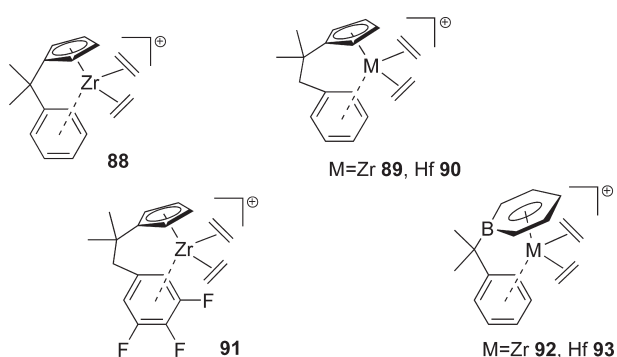


Follow-up theoretical work from Tobisch and Ziegler looked at the potential of Zr and Hf analogues to catalyze ethylene trimerization and tetramerization.^{152–154} Compared to Ti, the Zr and Hf analogues are predicted to undergo a more facile metallacycle growth to $\text{M}-\text{C}_6$ and $\text{M}-\text{C}_8$ cycles,¹⁵² which is most likely the rate-determining step of the reaction ($\text{M}-\text{C}_4 \rightarrow \text{M}-\text{C}_6$). Thus, Zr and Hf analogues of **84** have the potential to display a higher activity. Second, the ability of the metallacycles to undergo the product-releasing reductive β -hydride transfer step is reduced for the heavier group 4 metals. Taken too far, this effect would lead to metallacycle growth to long-chain polymers (see section 7). However, a middle ground exists where this effect should lead to 1-octene formation along with 1-hexene. According to the theoretical work of Tobisch and Ziegler, this is controlled by the difference ($\Delta\Delta G^\ddagger$) between the ΔG^\ddagger barrier to metallacycle

Scheme 16

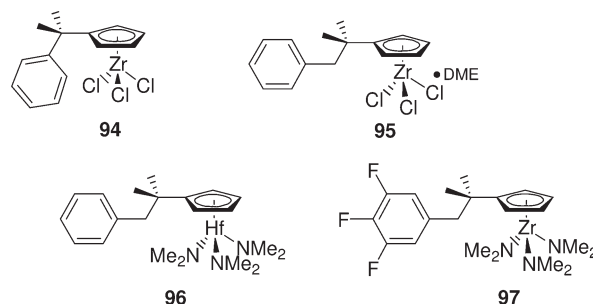


growth and ΔG^\ddagger for reductive β -hydride transfer (product release).¹⁵² Their work predicts, for instance, that Zr active species **88** should give rise to ~91% 1-hexene and 8% 1-octene. The Hf analogue is predicted to lead mostly to polymer; however, subsequent theoretical studies show that ligand modification, via bridge elongation or electron-withdrawing or -donating arene substituents, can be used to tune the $\Delta\Delta G^\ddagger$ value¹⁵³ and, hence, to selectively oligomerize ethylene. As such, catalysts of the form **89–91** were predicted to be selective for trimerization to 1-hexene. The final publication in the series analyzed the changes brought about by moving to boratabenzene analogues, such as **92** and **93**.¹⁵⁴ Again, these were predicted to be selective for the trimerization of ethylene. In related studies, other researchers have also analyzed the effect of coordination strength of the cyclopentadienyl substituent on trimerization selectivity, both for arene substituents and pendant oxygen and sulfur donors.¹⁵⁵ This model predicts that substituents having a dissociation energy from the titanium center of $<63 \text{ kJ} \cdot \text{mol}^{-1}$ will lead to multiple ethylene insertions (large-ring metallacycles), whereas dissociation energies of $>63 \text{ kJ} \cdot \text{mol}^{-1}$ will lead to selective trimerization.



Only very recently has experimental work been undertaken in an attempt to validate some of these predictions.¹⁵⁶ Unfortunately, the results are not nearly as positive as theory suggests they might be. Complexes **94–97** were prepared, which represent experimental precatalysts to active species **88–91**. In all cases, the catalysts led to $>90\%$ polyethylene formation after activation with MAO. In one case (complex **94**), selectivity to 1-hexene within the small amount of oligomeric products was

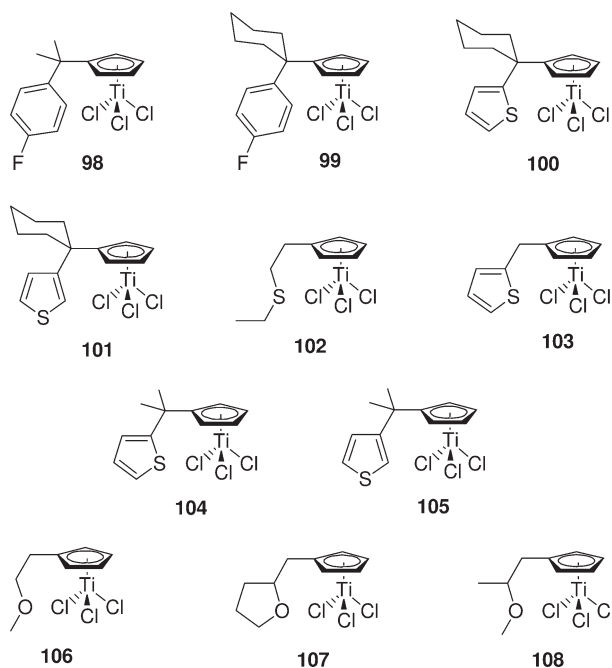
observed; however, polymer formation was still predominant. Mechanistic studies showed that 1-hexene is formed through a metallacycle mechanism with this catalyst and indicated that polymer formation is due to a separate active species operating via a conventional Cossee mechanism. Clearly, formation of the polymerization catalyst is the major activation pathway followed. Although one possible route into a Cossee mechanism from the M(IV) precursors was considered during the theoretical work, in reality there are any number of activation pathways that could proceed under experimental conditions.



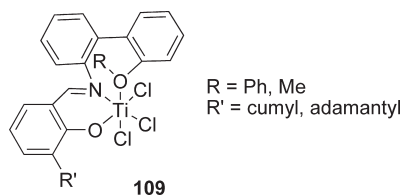
A number of modifications have been made to the parent titanium catalysts **84** in an attempt to find alternative or improved ligand systems. It is probably fair to say that these investigations have thus far met with limited success. *para*-Fluoro substitution of the arene group was tested through synthesis of complexes **98** and **99**.¹⁵⁷ Relative to the CMe₂-bridged parent without fluoro-substitution, complex **98** was much less active. The cyclohexyl-bridged analogue **99** performed similarly to the parent catalyst. It was concluded that fluoro-substitution disfavors, while the cyclohexyl-bridge favors, arene coordination. The result seems to be that the two offset each other. Overall though, introduction of fluoro-substitution is probably detrimental, because in the absence of it the cyclohexyl-bridged catalyst was one of the most active discovered in Hessen and co-workers' original work.¹⁴⁷

Keeping with the theme of a hemilabile-substituted cyclopentadienyl ligand, a number of researchers have investigated thioether- and thienyl-substituted Cp–Ti complexes. Huang and co-workers prepared complexes **100** and **101**, of which only **100** was selective for 1-hexene (TOF up to ca. 7900 h^{-1}).¹⁵⁸ It was postulated that this effect was due to the position of the sulfur donor, which can more easily interact with Ti in complex **100**. In unpublished work, McGuinness and Gibson also prepared and tested related complexes, **102–105**.¹⁵⁹ Only **103** gave appreciable 1-hexene selectivity (81% 1-hexene, 6400 h^{-1}), whereas **102** produced only polyethylene and **104** and **105** gave varying amounts of 1-butene and polymer (\pm trace 1-hexene). It is difficult to see any clear trends in this behavior, and it must be pointed out that CpTiCl₃, devoid of Cp-substitution, is also known to produce varying amounts of 1-hexene along with polyethylene.^{160,161} Indeed, a patent of 2005 reveals that similar selectivities and activities (82% 1-hexene, 4400 h^{-1}) can be achieved with only CpTiCl₃/AlMe₃/MAO.¹⁶² It is possible that the thienyl group in these complexes has very little influence on, or is actually detrimental to, trimerization selectivity in some cases. Huang and co-workers have also reported ether-functionalized cyclopentadienyl complexes **106–108**.¹⁶³ All three showed low activity for ethylene trimerization once activated with MAO, with selectivities ~90–95% 1-hexene and TOFs up to 2000 h^{-1} . These catalysts were benchmarked against CpTiCl₃, which was

not selective for 1-hexene under these conditions, therefore illustrating the beneficial effect of the pendant ether groups.



The most recent development in terms of titanium catalysis has moved away from Cp-based ligands. Researchers from Mitsui Chemicals have reported exceptionally active trimerization catalysts based around tridentate phenoxyimines with pendant oxygen donors, structure **109**.¹⁶⁴ Phenoxyimine (so-called FI) catalysts have been used with great success for α -olefin polymerization on early transition metals.¹⁶⁵ Their extension to selective oligomerization has likewise yielded excellent results. The best catalyst of structure **109** featured a methoxy pendant donor and a bulky adamantly substituent. In combination with MAO, a TOF in excess of $12 \times 10^6 \text{ h}^{-1}$ was achieved at 92% overall 1-hexene selectivity. The main byproducts, as with other highly active systems, are cotrimers of ethylene and 1-hexene. A second-order dependence on ethylene concentration was reported, suggesting that metallacyclopentane formation may be the rate-determining step with this catalyst.

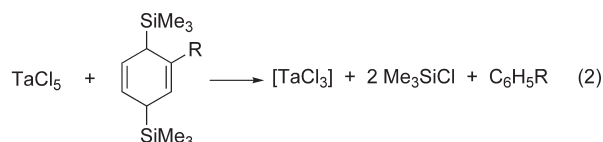


4.3. Tantalum Catalysts

Tantalum has long been known to promote metallacycle formation from olefins (see section 2).^{28,29} In 2001, Sen and co-workers showed that a combination of TaCl₅ and an alkylating agent (AlR₃, ZnR₂, SnR₄) is capable of trimerizing ethylene to 1-hexene with high selectivity.^{5,166} The activity of this system is rather modest (ca. 500 h^{-1}), but this has allowed some of the key intermediates to be identified by ¹H NMR spectroscopy. The initiating species was proposed to be Cl₃TaMe₂, which enters the catalytic cycle as shown in Scheme 16. This mechanism was supported by theoretical studies, which suggests that insertion of ethylene into the metallacyclopentane is the rate-determining

step.¹⁶⁷ 1-Hexene liberation is predicted to be a concerted process and is more facile than either 1-butene elimination or growth to a metallacyclononane, hence the selectivity to 1-hexene.

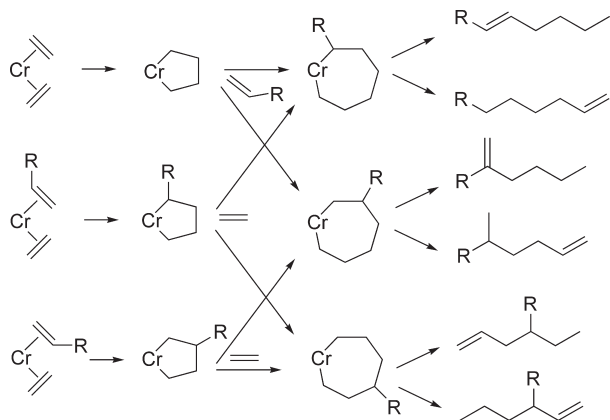
Researchers from the Sumitomo Chemical Company have recently reported an alternative reduction of TaCl₅ to the active species by utilizing bis(trimethylsilyl)cyclohexadienes (reaction 2).^{168,169} The resultant catalyst is reported to be more active than that resulting from alkylmetal reduction, and a patent filed on this work reports TOFs up to 2500 h^{-1} .¹⁶⁹ This work again supported a metallacycle mechanism, as the metallacyclopentane intermediate [Cl₃Ta(C₄H₈)] was detected by ¹H NMR spectroscopy. Sumitomo have filed a number of patents describing variants on the TaCl₅/MR_x system.^{170–172} These seem to be only slight modifications of Sen and co-workers' original system. Tantalum-based catalysts have not undergone anywhere near the level of development that chromium and titanium catalysts have and, as such, are probably worthy of further study. The introduction of well-designed organic ligands, as opposed to simple chloro ligation, may pay dividends for instance.



5. OLIGOMERIZATION OF HIGHER α -OLEFINS

The majority of the more active ethylene di-, tri-, and tetramerization systems also promote some degree of higher α -olefin incorporation to varying extents. This is normally manifest when the concentration of the primary product (e.g., 1-hexene for a trimerization catalyst) becomes high enough to compete with ethylene coordination and insertion.^{3,34,78,116,146} There are two stages of α -olefin incorporation possible: at the stage of metallacyclopentane formation or through insertion of the α -olefin into an already formed metallacycle (Scheme 17). It is unclear which pathway, if any, predominates, and most likely it is system dependent. The regiochemistry of the process is also highly dependent upon the metal/ligand combination, with some catalysts favoring linear cooligomers¹⁷³ and others leading to branched isomers.^{116,147} For the most part, this reaction represents a nuisance, effectively reducing the selectivity to the desired primary product. In some cases, however, this reactivity has been deliberately explored as a potential route to useful materials such as ω -substituted alkenes.^{173,174} Wass and co-workers have studied the cotrimerization of styrene and ethylene with Cr–PNP catalysts (ligands such as **31**, **33**, and **34**). As expected, increasing the concentration of styrene leads to increased selectivity to cotrimers (isomeric phenylhexenes) at the expense of 1-hexene formation. With ligand **31**, the major products were linear phenylhexenes (>80%), but with less sterically encumbered ligands, branched isomers became abundant.

Incorporation of more than one α -olefin during cooligomerization seems not to occur normally, although it has been observed in some cases.^{156,174,175} An example is the bis(carbene)pyridine chromium complex **110**, which cooligomerizes α -olefins with ethylene as illustrated in Scheme 18.¹⁷⁵ Accordingly, homo-oligomerization of α -olefins via metallacycles is rarely observed, but this may simply be because it is rarely attempted. The most notable example is selective α -olefin trimerization with chromium–triazacyclohexane complexes (**29**).^{73,176} The resulting

Scheme 17. Pathways Possible for α -Olefin Cotrimerization

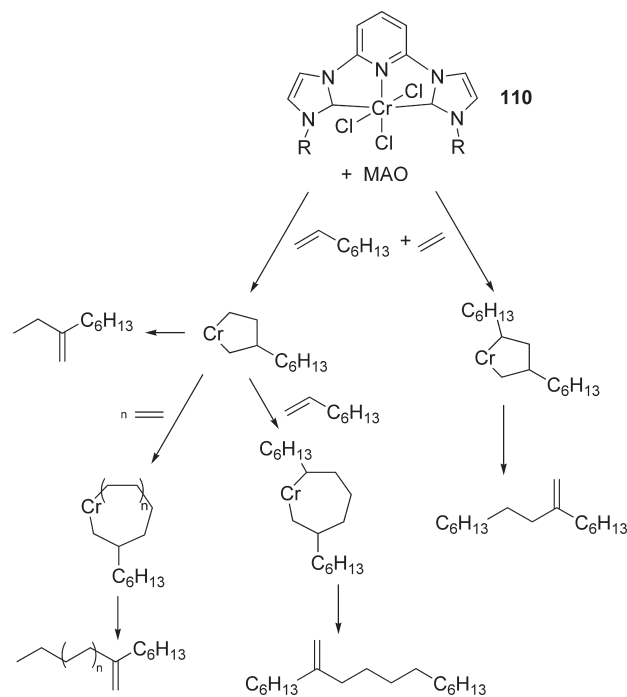
highly branched trimers are of some interest as synthetic lubricants. Recently, the homooligomerization of α -olefins with complex **110**/MAO has been demonstrated.¹⁷⁵ Long-chain olefins (1-octene) yield dimer almost exclusively, while shorter olefins (propene, 1-butene) lead to higher amounts of trimers and tetramers. Mechanistic studies support a metallacycle mechanism for the formation of these products. Kinetic measurements revealed a reaction that is first order in chromium and, unexpectedly, zero order in α -olefin, $r = k[\text{Cr}]$. There are two possible mechanistic explanations for such a rate equation (Scheme 19). The first is that formation of a bisolefin complex **111** is fast, followed by a rate-determining oxidative coupling to form the metallacycle (as such, **111** would represent the catalyst resting state, $k_2 < k_1, k_3$). Applying the steady-state approximation to **111**, the rate equation would be $r = k_2[\text{111}]$. The second possibility is that metallacycle formation is fast, followed by a rate-determining β -hydrogen shift and product release, in which case the catalyst resting state would be the metallacycles **112** ($k_3 < k_1, k_2$). In this case, the steady-state approximation would yield the rate equation $r = k_3[\text{112}]$. It is difficult to differentiate between these two possibilities.

6. OLIGOMERIZATION–POLYMERIZATION TANDEM CATALYSIS

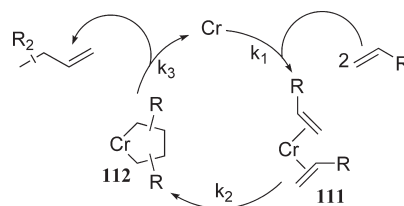
A technique that has received a lot of interest is tandem catalysis, wherein one catalyst oligomerizes ethylene to the desired comonomer (usually 1-butene) and a second catalyst copolymerizes ethylene and the comonomer to LLDPE (Scheme 20).¹⁷⁷ There are obvious advantages to such a one-pot approach, the principal one being that the comonomer does not need to be separately prepared, purified, and transported to site. Difficulties that must be overcome include interference between the two catalysts and matching of the activities such that the comonomer concentration can be maintained as desired. The production of branched polyethylene by tandem catalysis has been reviewed.¹⁷⁷ The work covered herein only covers those systems where the oligomerization component is one believed to be operating via a metallacyclic mechanism.

The earliest accounts of ethylene trimerization with chromium showed that the 1-hexene formed was incorporated into the polyethylene, which was the main product of the reaction.³² This represents an example of tandem catalysis starting from a single precatalyst; presumably a number of active species (trimerization and polymerization) form upon activation. It was later shown

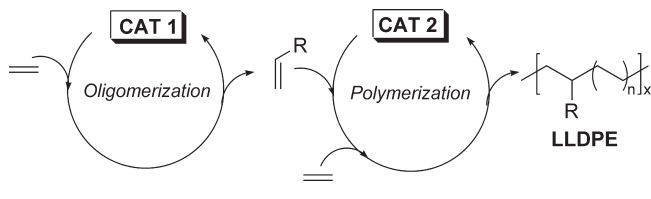
Scheme 18



Scheme 19



Scheme 20



that the system $\text{CpTiCl}_3/\text{MAO}$ behaves similarly, producing butyl-branched polyethylene from ethylene alone.^{160,161} Yet another example of this was patented by Phillips Petroleum, who treated the heterogeneous Cr/SiO_2 polymerization catalyst with pyrrole and AlEt_3 .¹⁷⁸ Few details of the amount or type of branching are given, but it is assumed that a portion of the chromium is homogenized through the action of pyrrole and AlEt_3 , which subsequently trimerizes ethylene to 1-hexene (section 4.1.1).

The use of a separate, highly selective trimerization or tetramerization catalyst in combination with a dedicated polymerization catalyst is the obvious next step. The development of highly active trimerization and tetramerization catalysts means that they are now able to keep pace with the polymerization component,

which are typically characterized by very high productivities. A number of groups have combined the Cr–SNS trimerization system (9, section 4.1.2) with zirconium metallocenes and constrained-geometry (Ti, Zr) polymerization catalysts (MAO activation).^{179–182} The open constrained geometry catalysts (CGCs) were shown to give better 1-hexene incorporation into the polymer (up to 6%), whereas Cp_2ZrCl_2 resulted in very little incorporation.¹⁷⁹ An interesting side effect noted in a number of cases is that an increase in the amount of trimerization catalyst led to a concomitant increase in polymerization activity. This is thought to be due to increased 1-hexene incorporation, which results in a more soluble branched polymer. As such, mass transport problems due to polymer precipitation are reduced somewhat. These catalyst components were also immobilized on silica, which means the two catalysts are not able to interact with one another.¹⁸¹ Such an interaction does not seem to be a problem with this combination of catalysts, however, but can lead to problems with other catalyst combinations as discussed later.

The trimerization catalyst **84** (section 4.2) has also been used along with titanium and zirconium CGCs.^{183,184} It was shown that the amount of butyl branching in the polymer can be controlled by adjusting the ratio of the two catalysts, and 1-hexene incorporation up to 14% was achievable. The authors also observed incorporation of C_{10} cotrimers (1-hexene + 2ethylene) into the polyethylene. When a zirconium-based polymerization catalyst was employed, there was evidence for some level of interaction between the two active sites, leading to catalyst deactivation in some instances.

A third general class of catalyst trialed in tandem oligomerization–polymerization are the Cr–diphosphinoamine systems (section 4.1.4). A patent from BP contains two examples of ligand **31**/Cr/MAO along with both a Ziegler catalyst and a zirconium CGC.¹⁸⁵ No real details are provided except to say that NMR analysis indicated butyl branching within the polymer. Sasol researchers likewise combined tri/tetramerization catalysts ($\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ /Cr/MAO) with zirconium metallocenes and CGCs.^{186,187} The optimum temperature for oligomerization was much lower than the optimum temperature for polymerization, so to circumvent this problem a temperature ramp was introduced. Trimerization and tetramerization were first produced at 50 °C before the temperature was raised for the copolymerization reaction. The polymer properties (degree of 1-hexene/1-octene incorporation) could thus be controlled by varying the amount of time that the reaction was held at the lower oligomerization temperature.

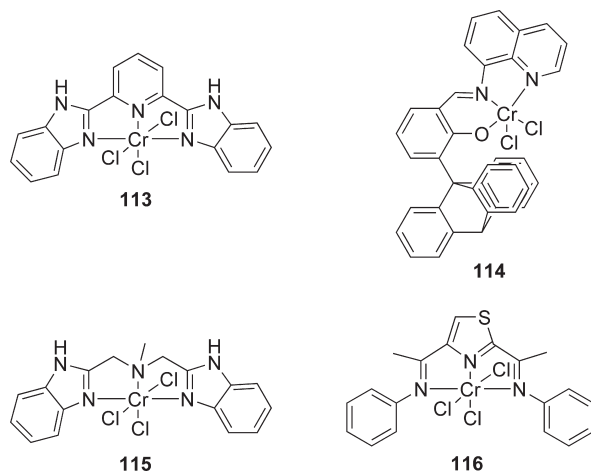
To the author's knowledge, there are no tandem oligomerization–polymerization processes operating commercially at this stage. However, this is an area likely to receive continued interest from both academic and industrial research groups.

7. AND BEYOND: EXTENDED METALLACYCLES AND POLYETHYLENE FORMATION

Selective oligomerization via metallacycles occurs when metallacycle decomposition (α -olefin formation) is more facile than further ethylene insertion at various metallacycle ring sizes. When this condition breaks down, the growth of large-ring metallacycles can be envisaged, which can be termed an extended metallacycle mechanism. The question then becomes how far can this process progress, and is it possible for high molecular weight polyethylene to form via metallacycles? This question is of fundamental importance, as such a process has long been

proposed as one model for polyethylene formation with the commercial Phillips catalyst (Cr on silica).^{76,188} This catalyst has been used on great industrial scale for over half a century; however, despite this, the mechanism of chain growth is still uncertain. There is no doubt some evidence for a metallacycle mechanism.^{76,189–191} There seems to be no obvious reason why large-ring metallacycles could not grow to high-molecular-weight polymer. Following the formation of the metallacyclopentane, the subsequent steps involve only migratory insertion of ethylene. As such, the growth process differs little from a conventional Cossee mechanism.

Over recent years, a number of reports have appeared that unequivocally demonstrate an extended metallacycle mechanism for the formation of higher α -olefins. All of these involve chromium catalysts. In the first such study, Gibson and co-workers described ethylene oligomerization and polymerization with catalysts **113** and **114** in combination with MAO.^{192,193} A Schulz–Flory distribution of α -olefins and low-molecular-weight polymer is formed, and deuterium labeling experiments ($\text{CH}_2\text{CH}_2/\text{CD}_2\text{CD}_2$ copolymerization) indicate a metallacycle mechanism. Gibson's group later reported the catalyst system composed of **115**/MAO, which converts ethylene to higher α -olefins and low-molecular-weight polyethylene ($M_n = 800\text{--}900$) with exceptional activity (TOF in excess of $14 \times 10^6 \text{ h}^{-1}$).¹⁹⁴ An unprecedented α -olefin distribution was observed in which the C_{4n} products ($\text{C}_8, \text{C}_{12}, \text{C}_{16}$, etc.) were more abundant than the C_{4n+2} products ($\text{C}_{10}, \text{C}_{14}, \text{C}_{18}$, etc.). This was explained by a metallacycle mechanism in which the metallacycle can occupy two distinct sites, arising from the nonplanarity of the central nitrogen donor. In the proposed model, the metallacycle prefers one of these sites, and elimination occurs preferentially from one of the two sites. More recently, researchers from Sasol have reported a similar catalyst (**116**) that behaves likewise.¹⁹⁵ Again, a model involving two different metallacycle sites provided the best explanation.



A further example of higher olefins and low polymer being produced by metallacycles is provided by complex **110**.¹⁹⁶ In this instance, the distribution of α -olefins showed another type of deviation from Schulz–Flory behavior. Depending upon the ligand substitution, the distribution was depleted in 1-butene or both 1-butene and 1-hexene. This revealed that metallacycle decomposition is retarded relative to further growth at the $\text{Cr}-\text{C}_4$ ($\pm \text{Cr}-\text{C}_6$) stage. This represents a qualitatively similar bias to that which must exist for ethylene tetramerization catalysts,

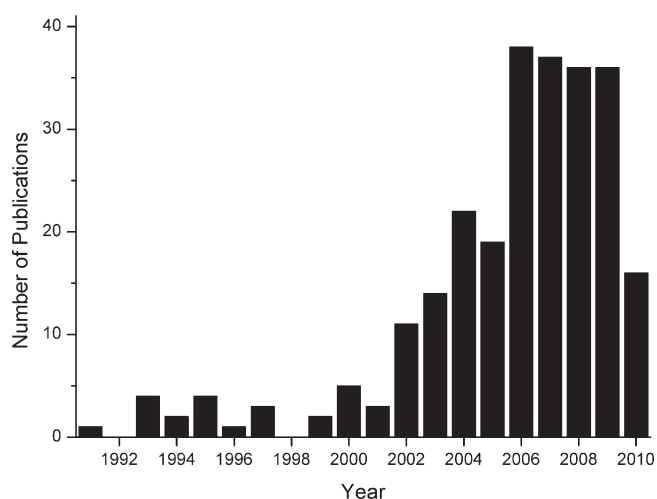


Figure 1. Ethylene trimerization and tetramerization publications by year (until June 2010).

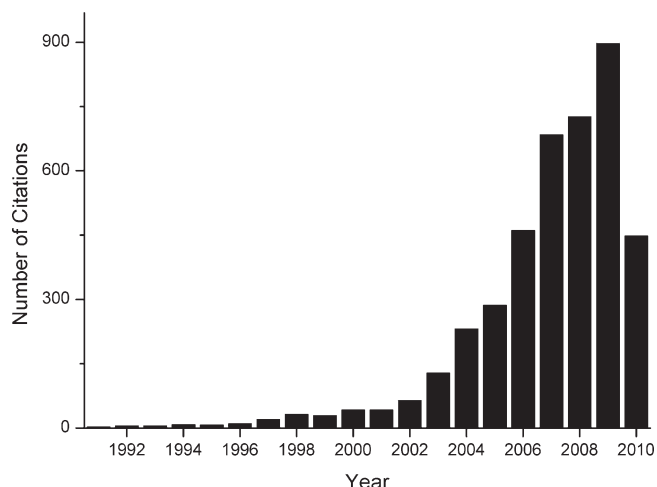


Figure 2. Citations by year to ethylene trimerization and tetramerization publications (until June 2010).

except in this case, higher metallacycle formation is competitive with Cr–C₈ product release.

It has also recently been shown that extended metallacycles, formed with a diphosphinoamine–chromium catalyst (section 4.1.4), are susceptible to chain-transfer reactions in the presence of ZnR₂.¹⁹⁷ This reaction was employed to prepare terminally Zn-functionalized α -olefins (C₁₀–C₂₂), which may be useful in the synthesis of other ω -functionalized α -olefins.

8. SUMMARY AND OUTLOOK

The past decade, and in particular the last four years, has certainly witnessed a tremendous increase in research activity in the field of olefin oligomerization via metallacycles. This is illustrated by Figures 1 and 2, which show the number of ethylene trimerization and tetramerization publications per year and the number of citations to these publications by year, respectively. This activity has been brought about by the very real needs of the chemical industry for more efficient routes to the polyethylene comonomers, in particular 1-hexene and 1-octene. While

selective production of 1-butene is a mature industry, 1-hexene and 1-octene production via this route is probably still in its infancy.

Recent developments have resulted in new catalysts displaying exceptional activity and selectivity. A case in point is the realization for the first time of ethylene tetramerization since this area was last comprehensively reviewed in 2004.⁵ At the same time, work has continued on the fundamental aspects of this chemistry, resulting in improvements to mechanistic understanding. Questions still remain, however, such as the structure and oxidation states of many of the chromium-based catalysts and the possibility of efficiently producing high-molecular-weight polymers via metallacycles. Even the mechanism of the Alphabutol catalyst (section 3.1) seems rather uncertain, despite the metallacyclic route being the “textbook mechanism” for this catalyst. A continued high level of interest in this field seems highly likely, driven by the desire both to answer these questions and to improve catalyst efficiencies still further.

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David McGuinness received his Ph.D. from the University of Tasmania in 2001 under the supervision of Professor Kingsley Cavell, before undertaking postdoctoral studies at the Institute for Technical and Macromolecular Chemistry (RWTH Aachen, Germany, 2001/02) with Professor Peter Wasserscheid and at Imperial College London (2002/03) with Professor Vernon Gibson. Following this, he worked for Sasol Technology (U.K.) based at the University of St. Andrews from 2003 to 2006. Since then, he has been an Australian Research Council QEII Fellow at the School of Chemistry, University of Tasmania. He is a past recipient of a British Council Chevening Fellowship, a Ramsay Fellowship, and a J. G. Russel award from the Australian Academy of Science. His research is focused on organometallic chemistry and catalysis.

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