Non Flory-Schulz ethene oligomerization with titanium-based catalysts

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1 General introduction

1.1 Introduction

Catalysis is the key to many chemical transformations. Catalytic processes are responsible for about 80% of all chemicals produced, and form the basis of nearly all processes with a throughput of more than 10,000 ton per annum\(^1\). For successful industrial implementation of a catalyst certain prerequisites have to be fulfilled. The ideal catalyst has to combine high efficiency (i.e. effective use of starting materials, and minimal waste emission\(^2\)), high selectivity (i.e. optimal conversion to the desired product\(^3\)), and high total turnover (i.e. amount of product formed per given amount of catalyst) with durability (e.g. low toxicity\(^4\)) and low overhead expenditure (i.e. cheap catalyst, and little maintenance). Understanding how catalyst structure and properties can affect these parameters, combined with chemical curiosity, is and will be the driving force for the future improvement and development of catalysis. Mutual efforts from industry and academia have made that the field of catalysis has grown from mere trial-and-error catalyst development to judicious design based on the rationalization of previous knowledge and theoretical background (when possible)\(^5\).

1.2 Transition metal catalysis

Transition metals are at the core of a wide range of catalyst systems\(^6\). In comparison with main group metals, transition metals have more orbitals available for interactions, and with different symmetry (d-orbitals). The possibility to distribute its valence electrons in nine valence shell orbitals that can interact with other groups simultaneously, allows the formation of both \(\sigma\)- and \(\pi\)-bonds with, for example, reactive substrates. Additionally, transition metals can combine specific functions, e.g. Lewis acidity, substrate activation, redox chemistry and polar bonds. This diversity is a key factor in imparting catalytic properties to transition metals and their complexes. The ability to accommodate inert spectator ligands, in addition to reactive moieties, forms the basis for innovative transition metal catalyst design. These ancillary ligands primarily control the configuration and conformation of reactive complexed intermediates, and thus catalyst selectivity. Variation of the properties, either steric or electronic or both, of such ligands offers the opportunity to tune catalyst properties. The wide range of possible spectator ligands, metal
oxidation states and coordination numbers provides a near infinite array of potential catalysts.

The unique character of the metal-carbon bond is another important element of (transition) metal-based catalysts, that has been exploited in many catalytic (and stoichiometric) metal-mediated transformations. Carbon is more electronegative than any (transition) metal and, hence, metal-carbon bonds principally have a polarity $\text{M}^{\delta^+}\text{-C}^{\delta^-}$, making the carbon atom susceptible to electrophilic, and the metal center to nucleophilic attack. The polarity of the M-C bond can be easily tuned by (1) the choice of metal, (2) the oxidation state of that metal, and (3) the properties of its spectator ligands. The wide range of available organometallic metal-alkyl species offers a broad spectrum of reactivity with various substrates to allow interesting opportunities for C-C, C-H, C-O, C-N, and C-X bond formation.

A very important application of C-C bond formation with organometallic catalysts is the polymerization and copolymerization of olefins, and, closely related, the oligomerization of olefins. Both processes will be discussed in more detail in the following sections.

1.3 Olefin polymerization

1.3.1 Polyolefins

In 1955 Ziegler found that the polymerization of ethene to high molecular weight linear polyethylene could be achieved with a TiCl$_4$-AlClEt$_2$ catalyst system. At about the same time Natta showed that it is possible to stereoselectively polymerize propene to isotactic polypropene with a closely related catalyst system. Shortly after these findings, mixtures of CrO$_3$ and SiO$_2$ were reported to effectively polymerize ethene to HDPE (High Density Polyethylene, ‘Phillips process’). Since these initial discoveries almost half a century ago, the quest for new catalysts which allow the cheaper manufacture of existing polyolefins, or afford new and/or better olefin polymers has never ceased. The production of polyolefins has witnessed a 100% increase in production volume over the past decade only. The growth has recently slowed down at an estimated worldwide annual production of 80 million tons (in 2000) for the olefin polymerization industry. With the current state of the art in polyolefin production, the properties of polyolefins can be varied within wide limits to provide not just substitutes but alternatives to currently available polymers, such as polyvinylchloride or polyacetates. The accessible range of stereo- and regioregularities and molecular weights of polyolefins allows for the manufacture of tailored polyolefinic materials with predetermined properties (e.g. hardness, toughness, stiffness or transparency).

Stereoselective homopolymerization of \(\alpha\)-olefins (e.g. propene, 1-hexene and styrene) affords a wide range of polymers (isotactic, syndiotactic, hemiisotactic and block polymers), each with typical properties. Isotactic polypropene is a stiff but brittle polymer, in contrast to syndiotactic polypropene which is a robust transparent material.
Also copolymers are of great practical interest, and their total production volume matches that of homopolymers\textsuperscript{15}. Flexible linear polyethene with short-chain branches (Linear Low Density Polyethylene, LLDPE) is obtained by copolymerization of ethene with C\textsubscript{4}-C\textsubscript{8} \(\alpha\)-olefins\textsuperscript{16}, and is predominantly applied in packaging and as thin films. Copolymerization of propene with ethene yields materials with lowered crystallinity\textsuperscript{17} to give access to EP-rubbers and heterophasic materials\textsuperscript{18}. Copolymerization of ethene or propene with cyclic monomers (e.g. cyclopentene or norbornene) affords amorphous highly transparent materials that can be used in specialty optical and medical applications\textsuperscript{19}.

Terpolymerization of ethene, propene and dienes yields EPDM (Ethene Propene Diene Monomer) elastomers with high resistance to light and solvents\textsuperscript{20}. Equally interesting are catalysts with living polymerization characteristics, which should be able to allow (elastomeric) block copolymers\textsuperscript{21}.

1.3.2 Mechanisms of olefin polymerization and active species
In classical heterogeneous Ziegler-Natta catalysts\textsuperscript{8,9} polymerization takes place at the dislocations and edges of TiCl\textsubscript{3} crystals\textsuperscript{22}. Cossee and Arlman proposed a mechanism of polymer chain growth by \textit{cis}-insertion of the olefin into a Ti-C bond (Scheme 1)\textsuperscript{23}, which is now generally accepted, and has been supported convincingly by fundamental studies (\textit{vide infra}).

![Scheme 1: Cossee-Arlman mechanism for polymerization](image)

Based on Natta's early ideas about the role of chiral surface sites in the formation of isotactic polyolefins\textsuperscript{24}, models were proposed to explain the induction of stereoregular polymer growth by the chiral environment of the catalytic centers on the crystal edges\textsuperscript{25}. In Figure 1 the incoming propene adopts the enantiofacial orientation which places the methyl substituent \textit{trans} to the polymer chain at the
incipient C-C bond (left; the Cl* atom determines the orientation of the growing polymer chain, \textit{trans} to Cl*). The \textit{cis} orientation (right) is disfavored.

![Figure 1: Model for the stereospecific polymerization of propene at a chiral titanium center on TiCl$_3$ edges](image)

Due to the non-uniformity of the active sites in heterogeneous catalysts, and the limited experimental access to structural details there is no direct proof for the structures proposed. Homogeneous olefin polymerization catalysts should eventually allow more direct observations of the catalytically active species, and hence, on the mechanism of chain growth and stereoccontrol$^{26}$.

Shortly after the synthesis of the first group 4 metallocenes$^{27}$, the use of these compounds as polymerization catalysts was investigated$^{28}$. Mixtures of Cp$_2$TiCl$_2$ and AlClEt$_2$ were found to polymerize ethene with moderate activity, but propene and higher \(\alpha\)-olefins were not polymerized at all. Breslow and coworkers$^{29}$ and Chien$^{30}$ proposed that ethene polymerization proceeds via olefin insertion into the Ti-C bond of a Cp$_2$Ti-R electron-deficient species. Initially, ligand exchange between aluminum and titanium gives Cp$_2$Ti(Cl)Et. Coordination of the Lewis acidic aluminum to the chloride (Ti-Cl) polarizes the Ti$^{\delta^-}$-Cl$^{\delta^-}$ bond to create an electron-deficient titanium Cp$_2$Ti$^{\delta^+}$R species, which readily inserts ethene (Scheme 2). This mechanism incorporates several features of the Cossee-Arlman mechanism: (a) the Lewis acidity of the metal center, and (b) the mutual \textit{cis} orientation of the metal-alkyl bond and the incoming monomer.

![Scheme 2: Proposed pathway for the polymerization of ethene by Cp$_2$TiR-Cl-AlCl$_2$R via \textit{cis}-insertion](image)
There was considerable debate about the nature of the active species. Various research groups advocated bimetallic halide-bridged titanium-aluminum intermediates as the active species involved\(^{31}\). Crystal structures containing both titanium and aluminum\(^{32}\) were obtained from reaction mixtures, but they are not conclusive as such since they represent degradation products. The possibility of the involvement of a cationic titanium active species \([\text{Cp}_2\text{TiR}]^+\) was suggested by Shilov and coworkers\(^{33}\), but the idea of ionic intermediates did not find widespread acceptance as the active species in olefin polymerization.

Interest in the cationic intermediate was revived by the discovery of Eisch and coworkers that \(\text{Ph-C≡C-SiMe}_3\) reacts with \(\text{Cp}_2\text{TiCl}_2\) in the presence of \(\text{AlMeCl}_2\) to give a cationic titanium vinyl complex \([\text{Cp}_2\text{Ti}\cdot\text{C(Ph)=C(Me)SiMe}_3]^+\), formally the product of alkyne insertion in the Ti-C bond of \([\text{Cp}_2\text{TiMe}]^+\)\(^{34}\). A year later Jordan and coworkers reported the synthesis of the ionic species \([\text{Cp}_2\text{ZrMe(L)}][\text{BPh}_4]\)\(^{35}\). This system is active in ethene polymerization, and provided the first experimental evidence that well-defined, cationic metallocene species are capable of olefin polymerization in the absence of aluminum alkyl activators. This and related findings\(^{36}\) established (alkyl)metallocene cations as crucial intermediates in homogeneous polymerization catalysis, and they are now fully accepted as the catalytically active species.

### 1.3.3 Activation of metallocene catalysts

The moderate productivity of homogeneous catalyst systems in ethene polymerization almost meant the end of research into and development of homogeneous olefin polymerization catalysts. In the early 1980's, this drawback was overcome by the discovery of methylaluminoxanes (MAO) by Sinn and Kaminsky\(^{37}\). Although water is a poison for Ziegler-Natta catalysts, addition of small amounts of water to the catalyst system may dramatically enhance the activity. This water-effect has been observed for the system \(\text{Cp}_2\text{TiEtCl/AlEtCl}_2\)\(^{38}\), and also for the normally inactive \(\text{Cp}_2\text{TiCl}_2/\text{AlMe}_2\text{Cl}\) system\(^{39}\). Sinn and Kaminsky observed that the normally inactive halogen-free \(\text{Cp}_2\text{ZrMe}_2/\text{AlMe}_3\) system could also be activated tremendously by addition of water\(^{37}\). The presumed formation of methylaluminoxane (MAO) by partial hydrolysis of \(\text{AlMe}_3\), to give oligomeric mixtures of \([\text{MeAlO}]_n\), was supported by its direct synthesis. Activation of \(\text{Cp}_2\text{ZrR}_2\) \((R = \text{Cl, Me})\) with the isolated MAO led to exceedingly active catalysts for ethene polymerization. Furthermore, metallocene catalysts activated with MAO were capable of polymerizing propene and higher \(\alpha\)-olefins in contrast to aluminum halide activated systems\(^{40}\).

MAO is supposed to initially methylate the metal-halide bonds to give a \(\text{Cp}_2\text{MMe}_2\) species (Scheme 3, reaction 1). Some of the aluminum centers in MAO are assumed to have a high tendency to abstract a methyl anion from these (dimethyl)metallocenes to give \([\text{Cp}_2\text{MMe}_3]^+\) species (Scheme 3, reaction 1), that are most likely stabilized by the \([\text{Me-MAO}]^-\) counteranion. These coordinative contacts are appropriately weak to give way, in the presence of (substituted) olefins, to olefin-
separated ion pairs that are required for polymer chain growth. Since its discovery, MAO has become the most commonly used activator for catalytic olefin polymerization.

The realization that a weakly coordinating anion is crucial for high catalytic olefin polymerization activity led to the development of other (non-aluminum-based) activators capable of generating weakly coordinating anions. The catalyst systems thus generated were called ‘single site’ metallocene catalysts. Large anions as \([B(C_6H_4R)]^- (R = H^{41}, 3-Et^{36g}, 4-F^{42})\) and carboranes, such as \([C_2B_{9}H_{12}]^{36g,43}\), were used as counterions, but they showed fairly strong interactions\(^{44}\) with the \([\text{Cp}_2\text{MMe}]^+\) cations. Although active in ethene polymerization, most of these catalyst systems did not polymerize propene or higher \(\alpha\)-olefins. A breakthrough was the introduction of the very weakly coordinating\(^{45}\) perfluorinated tetraphenylborate, \([B(C_6F_5)_4]^-\), as a counterion\(^{46}\).

![Scheme 3](image)

**Scheme 3:** Different routes for the activation of metallocene precursors for olefin polymerization

Reaction of \(\text{Cp}_2\text{ZrMe}_2\) with \([\text{PhNMMe}_3]\)[\(B(C_6F_5)_4]\) afforded ethene polymerization catalysts with exceptionally high activities and gave the first active ‘single site’ zirconocene catalysts for propene and higher \(\alpha\)-olefin polymerization (Scheme 3, reaction 2). To avoid the presence of the amine, alkyl-anion transfer with \([\text{Ph}_3\text{C}]\)[\(B(C_6F_5)_4]\] could be used to generate the same ion pair (Scheme 3, reaction 3)\(^{47}\).
As an alternative to the generation of cationic complexes, the strong Lewis acid B(C₆F₅)₃ could be used to abstract a methyl anion from Cp₂MMe₂ to give [Cp₂MMe][MeB(C₆F₅)₃] (Scheme 3, reaction 4)⁴⁸. Residual coordinative contacts between the cationic metal center and the anion via the abstracted methyl group have been identified⁴⁸bc,⁴⁹, but appear weak enough to allow olefin coordination to yield highly active polymerization catalysts.

An excellent review on cocatalysts for metal-catalyzed olefin polymerization was recently written by Marks and Chen⁵⁰.

1.3.4 Development of stereoselective metallocene catalysts

The use of MAO and perfluorophenyl boron species as activator in metallocene catalysis gave access to active propene (and higher α-olefin) polymerization catalysts. As Natta discovered, heterogeneous polymerization catalysts, formed from TiCl₃ and AlCl₃Et₃-x, can polymerize propene with high stereoselectivity (to isotactic polypropene)⁹. In general, simple homogeneous metallocene catalysts, e.g. Cp₂MMe₂/MAO, afford atactic polypropene⁵¹. Designing ligands that allow one enantiofacial coordination of the incoming monomer over the other⁵², Ewen and Brintzinger reported the first homogeneous metallocene precatalysts for stereoselective propene polymerization (Figure 2)⁵¹,⁵³. Due to conformational constraints the ethylenebis(indenyl) and ethylenebis(tetrahydroindenyl) ligands give the rac form of the corresponding so-called ansa-metallocenes⁵⁴ chiral structures with C₂ symmetry that are contained under catalysis conditions (note: the meso form is C₃ symmetric and affords atactic polypropene).

![Figure 2: Structures of rac-(en)(thind)₂MCl₂ and rac-(X)(ind)₂MCl₂](image)

Stereocontrol in these systems is similar as proposed for heterogeneous Ziegler-Natta catalysts (vide supra)²⁵. The indenyl* ligand determines the orientation of the growing polymer chain, and the incoming monomer adopts the enantiofacial orientation (trans) that minimizes the steric interactions between the polymer chain and the monomer (Figure 3)⁵⁵. Via this ligand-induced stereoselectivity, these ansa-bisindenyl group 4 catalysts give isotactic polypropene.
The stereoselectivity of these catalysts could not compete with that of heterogeneous Ziegler-Natta catalysts\textsuperscript{56}, especially at elevated reaction temperatures, but the introduction of $\alpha$- and $\beta$-substituents on the indenyl ligand has afforded homogeneous catalysts with similar stereoselectivity and molecular weight as heterogeneous Ziegler-Natta catalysts, albeit much more active\textsuperscript{57}.

The structure-properties relationships in metallocene catalysts, and the underlying mechanisms have been extensively investigated\textsuperscript{58}, and have led to homogeneous metallocene catalysts for syndiotactic\textsuperscript{59}, hemiisotactic\textsuperscript{60} and stereoblock\textsuperscript{61} polypropene.

\subsection*{1.3.5 Chain termination processes}

Two main mechanisms\textsuperscript{62} (Scheme 4) for chain termination in metallocene-catalyzed olefin polymerization are generally assumed: $\beta$-H transfer to metal\textsuperscript{57bc} and $\beta$-H transfer to monomer\textsuperscript{63}. When $\beta$-H transfer to monomer prevails, the rate of chain termination increases with increasing olefin concentration, but so does insertion, and hence, molecular weights will be independent on monomer concentration. For $\beta$-H transfer to metal, the rate of chain termination is olefin independent, and molecular weights will increase with increasing monomer concentration.

Another way to release the growing polymer chain is via chain transfer to an added transfer agent. Transfer agents can be used to control the molecular weight of the polymer. The most common transfer agent for that purpose is molecular hydrogen that has been successfully employed in Ziegler-Natta catalysis\textsuperscript{64}.

Other, but less frequently occurring, chain release processes are $\beta$-methyl transfer\textsuperscript{65} (quite common for metallocene catalysts with highly substituted cyclopentadienyl ligands) and transalkylation to the aluminium cocatalyst\textsuperscript{66} (in catalyst systems with high Al/metal ratio and low productivity).
Scheme 4: Chain termination via β-H transfer to metal and to monomer

1.3.6 Alternative ligand systems and group 4 catalysts

Group 4 polymerization catalyst research has mainly been focused on metallocenes, Cp\textsuperscript{R}MCl\textsubscript{2}. Nevertheless, numerous efforts have been made to explore the potential of other ligands and catalyst systems. Nowadays a wide range of non-metallocene group 4 catalysts has been prepared and tested in catalytic olefin polymerization (Figure 4\textsuperscript{13d}).

One particular modification of the cyclopentadienyl ligands can be achieved by insertion of a BY unit into the Cp ring to afford monoanionic boratobenzene ligands, (C\textsubscript{5}R\textsubscript{5}BY). The corresponding zirconium complexes (A) are highly active in ethene polymerization when activated with MAO\textsuperscript{67}. By changing the Y substituent on boron the relative rates of propagation and β-H elimination can be controlled and a range of polymer molecular weights is available with these versatile catalyst systems\textsuperscript{68}. Also substitution of a CH unit for a P atom has been investigated by various research groups\textsuperscript{69}. The resulting catalysts (B) show activities comparable to metallocene dichloride species.

For monocylopentadienyl group 4 complexes (C) moderate activities have been reported\textsuperscript{70}, especially for the syndiospecific polymerization of styrene with [Cp\textsuperscript{R}TiR\textsubscript{2}]\textsuperscript{+} species. An important class of olefin polymerization catalysts is formed by the so-called ‘constrained geometry catalysts’ (‘CGC’, D) developed by Dow and Exxon\textsuperscript{71}, based on Cp-amido ligands\textsuperscript{72}. The MAO activated procatalysts are highly active in homopolymerization of olefins as well as in copolymerization of ethene and higher α-olefins\textsuperscript{73}. Various groups have investigated the scope of the Cp-amido framework and its effect on catalysis\textsuperscript{74}. Replacing the NR group by an oxygen atom...
affords Cp-alkoxide ligands that have also been successfully applied as ligands for olefin polymerization active group 4 metal species (E)\textsuperscript{75}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Non-metallocene group 4 procatalysts for olefin polymerization}
\end{figure}

The high activity of the ‘constrained geometry catalysts’ prompted the development of other catalysts containing amide or other nitrogen based ligands. Monodentate amido\textsuperscript{76} and bidentate bisamido\textsuperscript{77} (F) group 4 complexes have been reported. Olefin polymerization activities for the bidentate complexes vary significantly and depend strongly on the chelate ring size and the nitrogen substituents\textsuperscript{78}. Also tridentate bisamido ligand systems containing a third neutral additional donor atom (N, O) have been prepared and introduced on group 4 metals (G). The resulting catalysts again vary strongly in olefin polymerization activities\textsuperscript{79}. The combination of an amido and an imine function gives a monoanionic six-electron donor ligand, isostructural and isoelectronic with a cyclopentadienyl ligand. These so-called
amidinate ligands (H) yield group 4 catalysts with moderate activity in olefin polymerization\(^{80}\). Amidinate ligands have also been employed in combination with other ligands such as Cp\(^{81}\) and amine ligands\(^{82}\). The latter systems show remarkably high activity for propene and 1-butene polymerization. Also β-diketimates, formally a higher homolog of amidinate ligands, have been introduced on group 4 metals (I), but only give moderately active catalysts\(^{83}\).

Besides nitrogen-based ligands, oxygen donor ligands have been used in group 4 olefin polymerization catalysis. Chelating bisphenoxide ligands (J) have given moderately to highly active catalysts for olefin homopolymerization\(^{84}\) and copolymerization of α-olefins with ethene\(^{85}\). Bisalkoxide ligands with one (K)\(^{86}\) or more (L)\(^{11d,87}\) additional donor atoms (N, O, S) have been shown to improve the olefin polymerization activity dramatically.

### 1.3.7 Group 3 metal and lanthanide catalysts

Neutral group 3 (Sc, Y) and lanthanide alkyl complexes are isoelectronic with cationic group 4 alkyl complexes. This analogy has been used in the design of group 3 and lanthanide catalysts for olefin polymerization. The potential advantage would be that they could be active as such, and would not require addition of a cocatalyst.

Ligand development for organoscandium and organoyttrium olefin polymerization catalysts has been following the general trends of group 4 catalysts, although the former are much less well explored\(^{88}\). Both scandium\(^{65c,72,89}\) and yttrium\(^{90}\) complexes containing Cp-based ligands have been prepared, but they exhibit low to moderate ethene polymerization activity. For yttrium also benzamidinate ligands have been employed affording catalysts with very low activity\(^{91}\).

![Figure 5: Cationic group 3 catalysts for olefin polymerization](image)

Lanthanide-based olefin polymerization catalysts have invariably been stabilized with substituted Cp analogs. The catalysts have been reported to show at best moderate activity\(^{92}\), although high initial activities have been observed\(^{93}\) (note: [Cp\(^*\)\(_2\)LnH]\(_2\) is the ethene polymerization catalyst with the highest initial activity reported).
Recent investigations in this area have afforded highly active cationic group 3 and lanthanide catalyst systems\(^94\), such as \([\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{NMe}_2]\text{Sc}(\text{CH}_2\text{Ph})]^+\) (Figure 5, M) and \([N,N'-\text{R}_2\text{-taen-N''-CH}_2\text{CH}_2\text{N}(t\text{-Bu})]Y(\text{CH}_2\text{SiMe}_3)]^+\) (N, R = Me, i-Pr; taen = 1,4,7-triazacyclononane).

### 1.3.8 Late transition metal catalysts for olefin polymerization

The impetus for late transition metal\(^95\) olefin polymerization catalysis is their decreased oxophilicity and greater functional group tolerance. These features would make such catalysts ideal for copolymerization of olefins with polar comonomers. The current advances in late transition metal chemistry have been recently reviewed\(^96\). This section will be limited to a discussion of the most important catalyst systems (Figure 6).

Group 6 heterogeneous catalysts play an important role in the commercial manufacture of polyethene. The Phillips catalyst consists of a silica support treated with CrO\(_3\), which is subsequently reduced to an, as yet elusive, low-valent chromium species\(^10\). This system is extremely active and offers the advantage of not requiring a cocatalyst. Homogeneous chromium catalysts have recently been reviewed\(^97\). The most active homogeneous chromium catalyst thus far is the Cp-amino Cr(III) compound (O) reported by Jolly and coworkers\(^98\). Recently, BASF patented some highly active chromium systems based on a substituted neutral 1,3,5-triazacyclohexane (tae, P) ligand on Cr(III)\(^99\). By varying the substitution pattern on the tac-ligand the catalyst system can shuttle between a polymerization\(^100\) or trimerization\(^101\) catalyst.

![Figure 6](image-url)

**Figure 6:** Late transition metal procatalysts for olefin polymerization
Few active group 8 and 9 catalysts have been reported. The most active polymerization catalysts are iron(II) species stabilized with a 2,6-bis(imino)pyridine ligand (Q) with highly substituted aryl substituents on the imino nitrogens. By decreasing the size of the ortho substituents the system can be converted into a very active olefin oligomerization catalyst. The corresponding cobalt(II) compound is the most active group 9 catalyst reported thus far, but its activity is a magnitude smaller than that of the iron(II) compound.

Group 10 catalysts with anionic [P,O] ligands (R), well-known for the Shell Higher Olefin Process (see section 1.4.3), can polymerize ethene under certain conditions. Crucial to the switch from oligomerization to polymerization is the removal of the phosphine ligand, or the use of more labile stabilizing ligands, such as pyridine or ylides. Recently, Grubbs reported nickel complexes with anionic [N,O] ligands (S) that are highly active in homopolymerization of ethene and copolymerization of ethene with polar comonomers. Another important class of group 10 polymerization catalysts is formed by nickel(II) and palladium(II) complexes with bulky diimine ligands (T). These catalysts are very versatile in their polymerization behavior. Block polymers, chain-end-controlled isotactic polypropene and ethene copolymers with polar comonomers belong to the possibilities. The diimine group 10 systems have been subject of both theoretical and experimental investigations.

1.4 Ethene oligomerization to higher linear α-olefins

1.4.1 Linear α-olefins

Apart from ethene and propene, higher (C_4-C_20) linear α-olefins have become increasingly interesting as monomer (to give poly-α-olefins) and as comonomer (to form LLDPE and HDPE) in catalytic olefin polymerization. Besides the use as polyolefin building blocks, higher linear α-olefins find their main applications as starting material for plasticizers (C_6-C_10) and surfactants (C_10-C_20).

The C_6-C_8 α-olefins can be hydrocarboxylated to give predominantly the linear carboxylic acids, which can be used as additives for lubricants together with their esters. Hydroformylation of C_6-C_10 α-olefins affords odd-numbered linear primary alcohols. They can, among others, be converted to polyvinylchloride (PVC) plasticizers.

Epoxidation of C_10-C_12 α-olefins opens a route to bifunctional derivatives or ethoxylates as nonionic surfactants. The C_14-C_16 α-olefins can be alkylated with phenols to yield alkylphenols, which can be employed as surfactants as well as lubricant oil additives.

Several processes are known to obtain α-olefins: wax-cracking of paraffins, oligomerization of ethene, dehydrogenation of paraffins, dimerization and metathesis of olefins, dehydration of alcohols and electrolysis of straight-chain carboxylic acids. Especially the second process, oligomerization of ethene, has been industrially
utilized to manufacture large amounts of linear α-olefins in the C_{4}-C_{20} range due to the abundance of ethene and the high product quality. In 1999, the worldwide annual production of higher α-olefins was about 2.5 million tons\textsuperscript{116}. The increasing need for α-olefins, especially as comonomer (C_{4}-C_{8}), causes the market still to expand, as illustrated by expansion plans of all major α-olefin producing companies.

1.4.2 Aluminum-catalyzed ethene oligomerization

The first ethene oligomerization process was developed by Ziegler (Alfen process) in the early 1950's. During extensive studies on organoaluminum compounds Ziegler discovered the Aufbaureaktion\textsuperscript{117}, a series of sequential repetitive olefin insertions into the Al-C bond (Scheme 5, equation 1), under high ethene pressure (100-400 bar) and moderate temperatures (100-150 °C). Relevant for the production of linear α-olefins was the observation that the insertion of ethene into an Al-H bond is reversible (Scheme 5, equation 2)\textsuperscript{118}, indicating that olefin elimination can occur. By varying pressure, temperature and reaction time Ziegler was able to induce displacement of the olefin (Verdrängung) affording triethyl aluminum (AlEt\textsubscript{3}) and three equivalents of α-olefins (Scheme 5, equation 3)\textsuperscript{119} at high temperature (250-400 °C) and low ethene pressure (10 bar).

\[
\text{AlEt}_3 + 3n \text{CH}_2\text{=CH}_2 \rightarrow \text{Al} \left[ \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \\ \vdots \\ \text{H} \\ \text{H} \end{array} \right]_n \quad (1)
\]

\[
\text{Al-H} + \text{RCH=CH}_2 \rightleftharpoons \text{Al-CH}_2\text{CH}_2\text{R} \quad (2)
\]

\[
\text{Al} \left[ \begin{array}{c} \text{H} \\ \text{H} \\ \vdots \\ \text{H} \\ \text{H} \end{array} \right]_n + 3 \text{CH}_2\text{=CH}_2 \rightarrow \text{AlEt}_3 + 3 \left[ \begin{array}{c} \text{H} \\ \vdots \\ \text{H} \end{array} \right]_{n-1} \quad (3)
\]

Scheme 5: Key steps in aluminum catalyzed ethene oligomerization

Unfortunately, the separation of the α-olefins from the AlEt\textsubscript{3} is extremely difficult, since the boiling points of AlEt\textsubscript{3} and 1-dodecene are close together, and most industrially interesting product mixtures contain significant quantities of 1-dodecene. The problem is often referred to as the Ziegler dilemma, since his group never found a commercially acceptable solution to this problem. Under the right conditions, e.g. at 200-250 °C, chain-growth and displacement can be carried out simultaneously\textsuperscript{120}. The AlEt\textsubscript{3} is continuously regenerated via displacement while chain-growth is proceeding. Small amounts of AlEt\textsubscript{3} (0.4 wt%) are needed which are hydrolyzed after reaction to facilitate separation. By reinsertion of the displaced higher α-olefins β-branched α-olefins are produced, but by utilizing
high ethene pressure (250 bar) formation of these branched olefins can be suppressed. This principle forms the basis of the Gulf/Chevron process, which is responsible for about 15% of the annual worldwide production.

In contrast to the Gulf/Chevron process, Ethyl Corporation uses a two-stage (one catalytic, one stoichiometric) α-olefin synthesis to overcome separation problems. The first stage is comparable to the Gulf process yielding predominantly C₄-C₁₀ α-olefins. These olefins are transalkylated with long-chain aluminum alkyls, liberating the higher α-olefins, whereas via chain-growth the remaining short-chain branched aluminum alkyls are converted into long-chain branched analogs in the stoichiometric part of the process. Via this two-stage α-olefin synthesis, Ethyl Corporation furnishes about 30% of the annual worldwide production of α-olefins.

1.4.3 The Shell Higher Olefin Process (SHOP)

The most important discovery made by Ziegler in 1952 was the observation that in the presence of nickel salts the alkylaluminum-catalyzed Aufbaureaktion is directed to yield mainly butenes. This phenomenon is often referred to as the ‘nickel effect’. These findings initiated an intensive investigation into organonickel chemistry. Wilke and coworkers were the first to observe the ligand effects on selectivity in nickel-catalyzed reactions. At Shell, ligand variations were extended to bidentate [P,O] chelates (Figure 7), and are now the basis for the Shell Higher Olefin Process (SHOP), which accounts for about 35% of the annual worldwide production of α-olefins made via ethene oligomerization. The SHOP-process is one of the larger industrial applications of homogeneous catalysis. In Table 1, the product distribution of α-olefin products manufactured via SHOP is compared with both aluminum-based processes (vide supra) and wax-cracking.

![Generalized structure of SHOP catalyst precursors](image)

**Figure 7:** Generalized structure of SHOP catalyst precursors

**Table 1:** Comparison of product distributions (wt%) of C₆-C₁₈ α-olefins

<table>
<thead>
<tr>
<th></th>
<th>Wax-cracking</th>
<th>Gulf/Chevron</th>
<th>Ethyl</th>
<th>SHOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Olefins</td>
<td>83-89</td>
<td>91-97</td>
<td>63-98</td>
<td>96-98</td>
</tr>
<tr>
<td>Branched olefins</td>
<td>3-12</td>
<td>2-8</td>
<td>2-29</td>
<td>1-3</td>
</tr>
<tr>
<td>Paraffins</td>
<td>1-2</td>
<td>1.4</td>
<td>0.1-0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Dienes</td>
<td>3-6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Monoolefins</td>
<td>92-95</td>
<td>99</td>
<td>&gt;99</td>
<td>99.9</td>
</tr>
</tbody>
</table>
Neutral nickel(II) complexes for ethene oligomerization

Nickel(II)-based catalysts with monoanionic \([P,O]\) chelating ligands for the oligomerization of ethene have been extensively studied\textsuperscript{127,128}, most notably by Keim and coworkers. It turned out that the \([P,O]\) chelating ligand controls the selectivity of the ethene oligomerization\textsuperscript{127a}, while the other ligands stabilize the complex. The importance of the chelate interactions on selectivity, was elegantly illustrated by Braunstein and coworkers\textsuperscript{127h}. By inducing hydrogen bond interactions with the oxygen atom of the \([P,O]\) ligand, \(\beta\)-H elimination became dominant over propagation, thus affording lower \(\alpha\)-olefins.

\[
\text{Ph} \begin{array}{c} \text{O} \\ \text{P} \\ \text{Ni} \\ \text{Ph} \end{array} \text{Ph} \quad \begin{array}{c} \text{Ph} \\ \text{O} \\ \text{P} \\ \text{Ni} \end{array} \text{Ph} \quad \begin{array}{c} \text{Ph} \\ \text{P} \text{Ph}_3 \end{array} \quad \begin{array}{c} \text{Ph} \\ \text{P} \text{Ph}_3 \end{array}
\]

\[
\text{Ph} \begin{array}{c} \text{O} \\ \text{P} \\ \text{Ni} \end{array} \text{Ph} \quad \begin{array}{c} \text{Ph} \\ \text{P} \text{Cy}_3 \end{array} \quad \begin{array}{c} \text{F}_3 \text{C} \\ \text{O} \\ \text{P} \\ \text{Ni} \end{array} \text{F}_3 \text{C}
\]

\[
\text{CH}_2=\text{CH}_2 / 70 ^\circ \text{C} \quad \text{- styrene}
\]

\[
\text{A} \quad \text{B} \quad \text{C} \quad \text{D}
\]

**Figure 8:** Evidence for nickel(II) hydride species

It is largely accepted that the active species in ethene oligomerization is a nickel(II) hydride. The mechanism for the hydride formation is supported by the reaction of the nickel(II)-phenyl species (A) with ethene to yield the corresponding hydride intermediate (B) and styrene (Figure 8, top)\textsuperscript{127d}, which could be detected by GC. In the case of complex C, in situ NMR studies indicated the existence of a nickel hydride\textsuperscript{127c}, whereas the stable nickel hydride D could be isolated and characterized\textsuperscript{127d}. Multiple ethene insertions into the Ni-H bond (followed by \(\beta\)-H elimination) gives a Flory-Schulz distribution of linear \(\alpha\)-olefins (Scheme 6).

Over the years many other monoanionic chelating ligands, e.g. \([P,N]\)\textsuperscript{129}, \([P,S]\)\textsuperscript{130}, \([S,O]\)\textsuperscript{131}, \([N,O]\)\textsuperscript{132}, \([\text{As},O]\)\textsuperscript{133}, \([O,O]\)\textsuperscript{134}, \([N,N]\)\textsuperscript{135} and \([S,S]\)\textsuperscript{136} chelates, have been investigated, mainly by Keim, Braunstein and Cavell.
1.4.5 Cationic group 10 ethene oligomerization catalysts

In general, the neutral catalytically active species require high reaction temperatures and pressure for the oligomerization of ethene. SHOP operates typically at 80-120 °C and 70-140 bar. Since the late 1960's, cationic Ni(II) allyl complexes were known to oligomerize and dimerize ethene. Later on, also cationic Pd(II) complexes (as well as PdCl$_2$) were found to oligomerize ethene. Keim and Tkatchenko found that neutral [P,O] chelates, which afford cationic nickel complexes, allow ethene oligomerization at much lower temperature and pressure. Similar palladium compounds were found to dimerize ethene to butenes. This discovery led to development of group 10 complexes with neutral chelating ligands, such as [N,N] (diimine, pyridylimine, and diamine) and [P,N], to provide highly active ethene oligomerization catalysts.
1.4.6 Group 8 and 9 based catalysts for ethene oligomerization

Very few active group 8 and 9 oligomerization catalysts have been reported in the literature, in contrast to the well-documented wealth of group 10 catalysts. In the early days of homogeneous catalysis, simple transition metal salts, such as RhCl$_3^{139bc,147}$, were studied and found to be active in the dimerization of ethene to butenes. For the Co(acac)$_3$/AlEt$_3$ system a selectivity of up to 99.5% 1-butene was reported$^{148}$. While the organometallic chemistry developed, new well-defined hydride and alkyl species of group 8$^{149}$ and group 9$^{150}$ were tested in catalytic ethene oligomerization. Only dimerization activity was found, indicating fast chain transfer in these catalyst systems. Until recently, the only active group 8 or 9 catalyst (Figure 9, U) for ethene oligomerization was reported by Braca and Sbrana$^{151}$ albeit with low activity.

![Figure 9: Group 8 and 9 ethene oligomerization catalysts](image)

In 1998, Brookhart$^{103}$ and Gibson$^{102b}$ reported highly active catalysts for ethene oligomerization based on iron and a neutral tridentate 2,6-bis(arylimino)pyridine ligand (Q). By varying the substitution pattern, especially on the ortho position, of the aryl groups the activity and selectivity can be tuned$^{152}$. Analogous Co systems have been reported to show similar reactivity but less active$^{153}$.

1.4.7 Early transition metal catalyzed ethene oligomerization

In the late 1950’s, titanium precursors, e.g. $R_n$TiCl$_{4-n}$ and Ti(OR)$_4$, were modified with organohalide aluminum compounds, $R_n$AlCl$_{3-n}$, and found to be active in ethene oligomerization$^{154}$ and dimerization$^{155}$. The active species and the mechanistic aspects of these titanium catalysts are not well-understood$^{156}$. Similar to ethene polymerization (see section 1.3.2), an empty coordination site at an electron-deficient titanium center, and a titanium-alkyl bond are fundamental requirements for ethene oligomerization, but different proposals have been put forth concerning the structure of the Ziegler-Natta catalyst active centers (Figure 10). They consist of either bimetallic systems$^{157}$, in which titanium is bonded to aluminum through halide or halide-alkyl bridges, but also monometallic titanium systems$^{23,158}$, and truly ionic species$^{159}$. Both the bimetallic$^{160}$ and monometallic$^{161}$ systems are backed up by
theoretical calculations. Recently however, it has been suggested that active species similar to those found in polymerization systems are present (vide infra, see section 1.3). Chain termination in these systems is presumed to occur via $\beta$-H transfer from the oligomer chain to coordinated ethene (see Scheme 4)\textsuperscript{162}. Reduction of Ti(IV) species to Ti(III) deactivates the oligomerization catalyst, and generates catalytically active polymerization centers (see section 1.3.2).

![Figure 10: Bi- and monometallic types of active centers](image)

The TiR\textsubscript{4}/X\textsubscript{n}AlR\textsubscript{3-n} systems can be improved by addition of ancillary ligands, such as ketones, amines and phosphines. These additives increase the selectivity to linear $\alpha$-olefins\textsuperscript{163} by increasing the electron density on titanium, which allows ethene to coordinate dominantly. The incorporation of higher $\alpha$-olefins is inhibited and, in consequence, suppresses the production of branched olefins. In addition to these electronic effects, steric effects of these ligands are able to increase the linearity of the olefins formed.

In the early 1970's, comparable zirconium/aluminum systems were tested in catalytic ethene oligomerization\textsuperscript{164}. The zirconium catalysts are, in general, more active and more selective than the titanium catalysts. However, a constant ethene supply is necessary to reach high selectivities to linear $\alpha$-olefins. As an advantage to the titanium catalysts, catalyst deactivation via reduction of zirconium does not seem to occur\textsuperscript{115a}. Deactivation of the zirconium species is assumed to proceed via disproportionation of two Zr-alkyl species to give inactive bimetallic Zr-alkyl-Zr species and alkane. Similar to titanium-based systems, donor ligands improve the performance of the zirconium/aluminum catalysts. These zirconium/aluminum/donor ligand catalyst systems were used by Idemitsu in a relatively small industrial process for $\alpha$-olefin manufacture\textsuperscript{165}.

The role of the added ligands, like the nature of the active species, is subject of debate. After the initial Idemitsu patents appeared, a vast number of donor ligands have been used, most notably by Idemitsu itself, in zirconium-based ethene oligomerization catalysts\textsuperscript{166}. Based on the similar activities for ZrCl\textsubscript{4}-ester adducts
and Zr(CH₂Ph)₄ in ethene oligomerization studies, Young reasoned that the ancillary ligands primarily serve to solubilize the ZrCl₄ to allow rapid interaction between the zirconium and the aluminum cocatalyst. However, recently zirconium-based systems (Figure 11) have been prepared in which catalyst activity and product distribution can be controlled by steric and electronic ligand variation suggesting active participation of the ancillary ligand.

A number of zirconocene-based catalysts have been found active in ethene oligomerization, including cationic species formed in situ in the absence of aluminum cocatalyst. The latter observation argues that an active cationic species, similar to that suggested for polymerization catalysts, is highly likely.

**Figure 11:** Zirconium-based ethene oligomerization catalysts

### 1.4.8 Inorganic heterogeneous catalysts for ethene oligomerization

Materials such as nickel oxide and nickel salts supported on silica and/or alumina have been reported to be active catalysts for the oligomerization of ethene. The activities and selectivities of these catalyst systems are strongly affected by product adsorption (on the support), and by isomerization and cooligomerization to produce branched olefins. Increasing acid strength of the silica-alumina support achieves higher activity per nickel site. Nickel oxide on an alumina support modified with sulfates proved to be a highly active and selective catalyst for ethene oligomerization, and variations of this system have been thoroughly investigated in the last five years.

Also nickel-exchanged zeolites as well as zeolites as such have been tested for ethene oligomerization activity. But these systems show poor selectivity to linear α-olefins. Recently, Jacobs and coworkers reported the successful use of zeolites as support for active and selective metallocene-based oligomerization catalysts.

### 1.4.9 Selective olefin oligomerization

All ethene oligomerization catalyst systems described in the foregoing part of this section afford a distribution of linear α-olefins (Flory-Schulz or Poisson). Very few oligomerization catalysts for selective olefin oligomerization, to a single olefin, except dimerization (of ethene or α-olefins), have been reported, some of which
have been employed industrially, most notably in the DIMERSOL process\textsuperscript{180}. Dimerization can either occur via an insertion-type pathway, i.e. two insertions followed by β-H elimination\textsuperscript{181}, or via a metallacyclic pathway involving oxidative coupling\textsuperscript{182} (Scheme 7).

\textbf{Scheme 7:} Different pathways for ethene dimerization to 1-butene

A similar metallacyclic pathway is proposed for the selective ethene trimerization to 1-hexene by chromium-based catalyst systems (mixtures of Cr salts with alkylaluminum compounds, and added ligands, especially imidazoles, or coordinating solvents, such as 1,2-dimethoxyethane)\textsuperscript{183}. A low-valent Cr species couples two ethene molecules to generate a chromacyclopentane, which subsequently inserts a third ethene molecule to give a chromacycloheptane (Scheme 8)\textsuperscript{184}. From the latter, 1-hexene is formed via β-H elimination (or 1,5-H shift) and reductive elimination to regenerate the low-valent Cr species\textsuperscript{98}. Recently, triazacyclohexane-based chromium precursors activated with MAO\textsuperscript{101}, TaMe\textsubscript{2}Cl\textsubscript{3}\textsuperscript{185} and (arene)\textsubscript{2}VX (X = Cl, Br, [BF\textsubscript{4}]\textsuperscript{-})\textsuperscript{186} systems were also found to effectively affect this unique and intriguing reaction, presumably via the same pathway.

\textbf{Scheme 8:} Proposed catalytic cycle for selective ethene trimerization by Cr-based catalysts
1.5 Switching from ethene polymerization to oligomerization activity

In the previous two sections, 1.3 and 1.4, we have encountered various systems that can be tuned to either ethene polymerization or oligomerization activity (1) by controlling the reaction conditions or (2) via subtle, easily accessible ligand variations. For example, Ziegler discovered that the system TiCl₄-AlClEt₂ polymerizes ethene to high molecular weight polyethene⁸, but by controlling the reaction conditions (temperature, ethene pressure) the same system can be switched to a moderately active ethene oligomerization¹⁵⁴ or dimerization catalyst¹⁵⁵.

Ligand variation, potentially, offers a more elegant route to govern interconversion between polymerization and oligomerization active species. The key to a successful switch is control over the relative rates of chain propagation (k_p) and chain termination (k_t). Increasing k_t over k_p will lower the molecular weight of the polymer, and eventually lead to the production of α-olefins. Recently, a range of transition metal catalysts have been developed that readily alternate between ethene polymerization and oligomerization activity by changing the steric or electronic properties of the ancillary ligand (Figure 12).

The diimine Ni(II) and Pd(II) catalysts (A) can be easily tuned by the ortho substituents on the aryl rings. Bulky substituents, such as iso-propyl, effectively block the axial positions¹¹⁰, and suppress the chain termination transition state, to afford polyethene¹⁰⁶. The sterically undemanding ortho methyl groups are not adequately bulky, and β-H elimination can readily take place to give a distribution of α-olefins¹⁴⁴. The ortho aryl substituents in the bis(imino)pyridyliron(II)¹⁸⁷ and cobalt(II) complexes (B) exert a similar steric control on the rate of chain termination, and thus on product formation¹⁰²,¹⁰³.

The substituents on the 1,3,5-triazacyclohexane ligand in the tac-chromium systems (C) presumably perform steric control in reverse fashion. Linear alkyl chains (C₁-C₁₂) on the nitrogen atoms lead to moderately active ethene polymerization catalysts¹⁰⁰. Substituents on the 2-position of the alkyl chain increase the steric congestion at the metal center and convert the catalyst into a selective ethene trimerization catalyst (note: α-olefins are exclusively trimerized, also with straight chain alkyl nitrogen substituents¹⁰¹). In these systems, activity can also be tuned by the reaction conditions. Similar effects are observed in (η⁵-C₅H₅CH₂CH₂PR₂)CrCl₂/MAO ethene oligomerization systems¹⁸⁸, in which the molecular weight of the α-olefins produced decreases with increasing steric bulk of the phosphor substituents¹⁸⁹.

As a last example, the relative rates of chain propagation and chain termination can be controlled by electronic substituent effects (although steric effects cannot be completely excluded). By changing the boron substituent of di-iso-propylamine to ethoxide (or phenyl) in boratobenzene zirconium complexes (D), the rate of β-H elimination increases, which results in the formation of lower molecular weight oligomers⁶⁸ instead of polyethene⁶⁷.
1.6 Aim of this investigation

Group 10 compounds with anionic \([\text{P},\text{O}]\) ligands are well-known to oligomerize ethene and play a central role in SHOP\textsuperscript{104}. There have also been reports that SHOP-type oligomerization catalysts can polymerize ethene under certain conditions\textsuperscript{105}. Crucial to the formation of high molecular weight polymers rather than oligomers is the use of labile groups \(L\), such as pyridine or ylides, or the effective removal of phosphorus-based \(L\) groups\textsuperscript{100}, such as \(\text{PPh}_3\). In other words, the catalytic activity of the \(\text{Ni(II)}\) species can be controlled by the nature of the neutral ancillary group \(L\).
Similarly, the presence of weak donor ligands, such as aromatic ethers and amines, can convert group 4 propene polymerization catalysts $[\text{Cp}_2\text{MMe}]^+$ into oligomerization catalysts, albeit with a significant reduction in activity, since these donor ligands effectively compete with the olefinic substrate for the coordination site required for chain growth\textsuperscript{36c,f}.

We became interested in the possibilities to tune the properties (activity, selectivity and stability) of catalytically active species by neutral donor moieties. We decided to combine this idea with the concept of ligand-controlled catalyst reactivity, and set out to design ancillary ligands substituted with neutral donor-functionalized side chains that provide the opportunity of intramolecular coordination. The chemistry of cyclopentadienyl complexes of this type\textsuperscript{191} (e.g. $\text{Cp-N}$\textsuperscript{192}, $\text{Cp-O}$\textsuperscript{193}, $\text{Cp-P}$, $\text{Cp-As}$ and $\text{Cp-S}$\textsuperscript{194}) and their potential application as catalysts present a rapidly growing area of research. As the cyclopentadienyl-based catalyst systems of interest, we choose cationic monocyclopentadienyl titanium species, $[\text{CpTiR}_2]^+$.

These half-sandwich titanium complexes show interesting catalytic activity, most notably in the syndiospecific polymerization of styrene. Ishihara and coworkers were the first to report that syndiotactic polystyrene, a new macromolecule at that time\textsuperscript{195}, could be produced with high stereoregularity and yield under conventional conditions using half-sandwich titanium compounds activated with MAO\textsuperscript{196}. Syndiotactic polystyrene has become an important engineering plastic since\textsuperscript{197}, and many publications and patents have appeared on the subject\textsuperscript{198}. Various monocyclopentadienyl titanium complexes with chelating Cp ligands with neutral oxygen\textsuperscript{199} and nitrogen\textsuperscript{200} donor moieties have been prepared (Figure 14), and the effect of the $\pi$-donor on catalyst activity was studied. The presence of the tethered amino groups has clear, but not spectacular, effects on olefin polymerization reactivity of these complexes (lower activity and stereoselectivity for styrene polymerization, and higher activity in ethene and propene polymerization, compared to unsubstituted $\text{CpTiCl}_3$).
Recently, the catalyst \([\text{Cp}^*\text{TiMe}_2][\text{MeB(C_6F_5)_3}]\) was found to display interesting olefin polymerization activity with ethene and propene in toluene. Bochmann and coworkers reported the living polymerization of propene to high molecular weight atactic polypropene\(^{201}\), and Pellecchia and coworkers showed that polyethene produced by this catalyst contains considerable amounts of \(n\)-butyl side chains\(^{202}\). It was suggested that the catalyst is partly converted to a species that trimerizes ethene to 1-hexene, which is then incorporated into the polymer. The latter observation is very interesting, because it indicates that \([\text{CpTiR}_2]^+\) species can be transformed, from polymerization into oligomerization (i.e. trimerization) catalysts under certain conditions.

We sought ways of stabilizing electron-deficient half-sandwich titanium cations in order to study the catalytically active species, but also their reactive properties. To this purpose, we introduced (neutral) aromatic substituents on the cyclopentadienyl ligand, which have the potential of acting as weakly and reversibly coordinating ligands to the titanium center. The labile character of aromatic coordination to titanium has been previously demonstrated. Baird and coworkers showed that \([\text{Cp}^*\text{MMe}_2]^+\) cations \((\text{M} = \text{Ti}, \text{Zr}, \text{and} \text{Hf})\) can bind arene solvents (benzene, toluene, xylenes, mesitylene, styrene) reversibly\(^{203}\), and that this interaction is significantly weaker for Ti than for Zr and Hf\(^{204}\). The feasibility of intramolecular arené coordination was suggested by observations of Chien and Rausch on the \((\eta^5\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{Ph})\text{TiMe}_3/[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\) system, where NMR evidence was obtained for \(\eta^6\)-coordination of the arene moiety in the thermally labile cationic dimethyl species\(^{205}\).

For our studies on cyclopentadienyl-arene systems, we decided to use benzyl-substituted Cp ligands of general formula \([\text{C}_5\text{H}_3\text{R-CR'}_2\text{-Ar}]\), which can be easily prepared by reaction of the appropriate 3-R-6,6-R’-fulvene with aryl lithium to afford lithium salts of the desired ancillary cyclopentadienyl ligands. The wide range of suitable fulvenes and aryl lithium salts gives access to a readily available library of ancillary ligands. Introduction of the ligands on titanium(IV) and subsequent derivatization are straightforward. During the course of this investigation, other groups reported the preparation of related bis–\(^{206}\) and monocyclopentadienyl\(^{207}\) group 4 metal complexes and their properties in catalytic olefin polymerization\(^{208}\).
1.7 Survey of the thesis

In the foregoing part of Chapter 1, olefin polymerization and ethene oligomerization with transition metal-based catalysts is discussed. A synopsis of catalyst systems that can switch from olefin polymerization to oligomerization activity is given together with the aim of the investigation described herein.

In Chapter 2, the synthesis and characterization of \((\eta^5-C_5H_4CMe_2Ar)TiR_3\) (Ar = Ph, 3,5-Me_2C_6H_3; R = Cl, Me, CH_2Ph, CH_2CMe_3, CH_2SiMe_3) complexes are described. In addition, the thermolysis of the trialkyl complexes \((\eta^5-C_5H_4CMe_2Ar)Ti(CH_2R')_3\) (R' = Ph, CMe_3, SiMe_3), leading to ortho cyclometalation of the ancillary cyclopentadienyl ligand, and a kinetic study of this process are presented. The thermal decomposition shows simple first-order kinetics in the starting material. The respective rates of thermolysis for the different alkyl compounds show some aberrations from previously reported data for similar compounds, and a tentative explanation is provided. Deuterium labeling studies indicate a pathway involving an alkylidene intermediate, and the selectivity of alkylidene formation and the subsequent C-H addition are discussed.

Chapter 3 covers the generation of the cationic complexes from the neutral alkyl precursors activated with B(C_6F_5)_3 and [Ph_3C][B(C_6F_5)_4] to give initially cationic ansa-\([(\eta^5,\eta^6-C_5H_4CMe_2Ar)TiR_2]^+\) species (Ar = Ph, 3,5-Me_2C_6H_3; R = Me, CH_2Ph). For \([(\eta^5,\eta^6-C_5H_4CMe_2-3,5-Me_2C_6H_3)TiR_2][RB(C_6F_3)]\) in bromobenzene, thermal decomposition gives a dimeric Ti(III) dicationic species. The pathway involves titanium-boron-alkyl scrambling, reduction from Ti(IV) to Ti(III) and solvent C-Br bond activation. The Ti(III) dimer is the first structurally characterized example of ansa-\(\eta^5\)-cyclopentadienyl-\(\eta^6\)-arene ligand coordination. The cationic species \([(\eta^5,\eta^6-C_5H_4CMe_2Ph)Ti(CH_2Ph)_2]^+\) displays rapid ortho cyclometalation of the ligand at ambient temperature to yield \([(\eta^5,\eta^1-C_5H_4CMe_2C_6H_4)Ti(CH_2Ph)]^+\). Deuterium labeling studies show that in the cations ortho cyclometalation proceeds via direct \(\sigma\)-bond metathesis, in contrast to the pathway via an alkylidene intermediate identified for the neutral species.

Subsequently (Chapter 4), the catalytic olefin conversion properties of the cationic dimethyl species, described in the previous chapter, are investigated. Interestingly, ethene is found to be trimerized with high selectivity to 1-hexene. No significant polymerization activity for propene and styrene is observed. The catalyst system \((\eta^5-C_5H_4CMe_2Ph)TiCl_3/MAO\) is tested under various conditions in selective ethene trimerization. This catalyst shows >95% trimerization selectivity affording mainly 1-hexene and a C_{10} fraction (cotrimers of ethene and 1-hexene, mainly 5-methylnon-1-ene). The effect of the aryl group (Ar = Ph, 4-MeC_6H_4, 3,5-Me_2C_6H_3) on activity and selectivity is discussed (extra aromatic methyl groups lead to a decrease in activity), together with the influence of solvent and activator. The selective ethene trimerization can be explained by assuming a mechanism involving titanacycloalkane intermediates. Oxidative coupling of two ethene molecules to a formal Ti(II) intermediate gives a titanacyclooctane. Subsequent insertion of ethene
followed by β-H elimination affords 1-hexene and regenerates the Ti(II) species. The presence of the aryl group attached to the cyclopentadienyl ligand is deemed crucial in the formation of the species active in trimerization.

In Chapter 5, the effect of ligand variations on the activity and the selectivity of the selective ethene trimerization process is presented. The results indicate that the bridging moiety between the cyclopentadienyl and arene group is of crucial importance for selective ethene trimerization, since only CR₂ groups (R ≠ H) afford trimerization catalysts (the most active with a cyclohexyl-based bridge [(CH₂)₅]C). Additional substituents on the cyclopentadienyl ligand (CMe₃, SiMe₃) can improve both activity and selectivity. The substituents are also effective in increasing the 5-methylnon-1-ene content in the C₁₀ fraction, giving a higher overall α-olefin content. The effect of the bridging group combined with that of cyclopentadienyl substituent is found to be roughly additive, and leads to activity improvements of 61% for the catalyst {η⁵-(3-SiMe₃)C₅H₅C[(CH₂)₅]Ph}TiCl₃/MAO. Surprisingly, combinations of cyclopentadienyl and aryl substituents, the latter previously found to decrease activity, give very active catalysts with a 93% improved activity for [η⁵-(3-SiMe₃)C₅H₅CMe₂-3,5-Me₂C₆H₃]TiCl₃/MAO with respect to its unsubstituted analog. The introduction of a second pendant arene group on the cyclopentadienyl ring eventually gives the catalyst system [η⁵-C₅H₃-1,3-(CMe₂Ph)₂]TiCl₃/MAO, which, interestingly, displays a constant trimerization activity in time over at least 2 h.

1.8 References and notes


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(51) The catalyst system \(\text{Cp}_2\text{TiPh}_2/\text{MAO}\) was found to produce isotactic PP at low reaction temperatures (-50°C), see: Ewen, J.A., *J. Am. Chem. Soc.* **1984**, *106*, 6355
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