

Metallocene Catalysts for Olefin Polymerization

Christoph Janiak

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104

Freiburg, Germany

Dedicated to Prof. Dr. Roald Hoffmann on the occasion of his 60th birthday.

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Abbreviations used

Bu butyl

Cp	cyclopentadienyl, general
Et	ethyl
Flu	fluorenyl
Ind	indenyl
IndH ₄	tetrahydroindenyl
MAO	methylalumoxane
Me	methyl
PE	polyethene
PP	polypropene
THF	tetrahydrofuran
TMA	trimethylaluminum

1. Introduction

Bis(cyclopentadienyl)group IV metal complexes are currently introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins.^{†1,2,3,4} Ziegler-Natta catalysis means the rapid polymerization of ethene and α -olefins with the aid and in the coordination sphere of a metal catalyst, operating at low pressures (up to 30 atm) and low temperatures (less than 120 °C). Among the group IV metallocenes of titanium, zirconium, and hafnium, the zirconocene complexes deserve the most interest both academically and industrially as their combination of properties gears them towards application (the titanocene

[†] The unspecified term *cyclopentadienyl ligands* (Cp) or *cyclopentadienylmetal complexes* is meant here to include substituted derivatives of the C₅H₅ parent ligand, such as C₅R₅ and also the indenyl and fluorenyl system, respectively the complexes thereof. If *the* parent cyclopentadienyl ligand or its metal compound is meant exclusively it is specifically stated by giving the formula C₅H₅ or (C₅H₅)_mML_n, respectively.

catalysts are unstable at conventional polymerization temperatures, the hafnium systems are too expensive). Hence, the so-called "metallocene catalysts" are mostly zirconocene derivatives, with zirconocene dichloride (**1**) being the parent system.⁵ Their development as practical polymerization catalysts is the first large-scale industrial application for the long known and well developed class of metallocene complexes.⁶ About all the fascinating organometallic chemical aspects in metallocene catalysis, the key aspect which earned them their enormous industrial research input is that group IV metallocene catalysts make polymers accessible which cannot be produced by conventional Ziegler-Natta catalysts, the polymerization of cyclic olefins without ring-opening being one remarkable example.^{‡7,8}

The fortuitous discovery of the iron derivative, ferrocene (C₅H₅)₂Fe,⁹ was a milestone in chemistry. The recognition and explanation of the remarkable structural and bond theoretical properties of ferrocene and the metallocenes at large by *Fischer*, *Wilkinson*, *Woodward*, and *Dunitz*,¹⁰ culminated in the award of the 1973 Nobel prize for *Fischer* and *Wilkinson* and established the study of direct metal-carbon bonds as an independent discipline, *Organometallic Chemistry*, as we know it today. Ever since, the cyclopentadienyl ligand has played a key role in the development of this field.¹¹ Cp complexes (π or σ bonded to the central atom) are now known for all main group and transition metals and semi-metals, as well as for the lanthanoid and the accessible part of the actinoid series. It is estimated that more than 80% of all known organometallic complexes of the transition metals contain the cyclopentadienyl fragment or a derivative thereof.¹² Yet, it was just recently, since about 1991 that an industrial

[‡] In this article, we will only cover the actual metallocene or *bis*(cyclopentadienyl)metall catalysts. The half-sandwich or *monocyclopentadienyl* group IV complexes used predominantly for syndiotactic styrene polymerization ⁷ and the "constrained geometry" or "Dow catalysts", R₂Si(Cp)(NR)MCl₂, containing the silyl-bridged cyclopentadienyl-amido ligand ⁸ are not included here.

application of this important class of compounds finally materialized with the zirconocene complexes as (pre-) catalysts for the Ziegler-Natta polymerization of olefins.

From 1984/1985, when the stereoselective polymerization of propene with zirconocene catalysts was first reported (see section 2), the synthetic, structural, mechanistic and applied research on metallocene catalysts has been highly visible in organometallic chemistry. A central piece of work in zirconocene catalyzed polymerizations of α -olefins was the elucidation of ligand effects, the correlation of the steric situation at the Cp-ligand with the polymer parameters, such as molar mass, molar mass distribution, comonomer insertion and distribution, and especially the tacticity (cf. section 7). With metallocene catalysts the polymer parameters can be tailored through a rational ligand design at the transition metal center (cf. section 7). Figure 1 gives a schematic overview on the most important ligand modifications.

The zirconocene complexes are not catalytically active by themselves but require the action of a cocatalyst. The cocatalyst directly associated with their application oriented development is methylalumoxane, abbreviated as MAO, whose composition and function is detailed in section 3. The novelty of metallocene versus classical Ziegler-Natta catalysis is best summarized in the word "single-site catalyst". This means that the active catalytic sites in the molecular zirconocene species are almost identical, whereas classical Ziegler-Natta catalysts are heterogeneous not just by the phase (as solid state catalysts) but also by their composition in having active sites with different environments at corners and edges on the solid surface.^{13,14} As a consequence of a single-site catalytic species, molecular mass distributions (M_w/M_n) in Ziegler polymerization down to about 2, the statistical lower limit for a Schulz-Flory distribution, can be reached with metallocene catalysts.¹⁵ Metallocene catalysts are sometimes also termed "homogeneous" referring both to their solubility and to their single-site character. In terms of their solubility, such a description may be slightly misleading, however, since for the industrial applications in slurry or gas phase processes and to gain control over the polymer

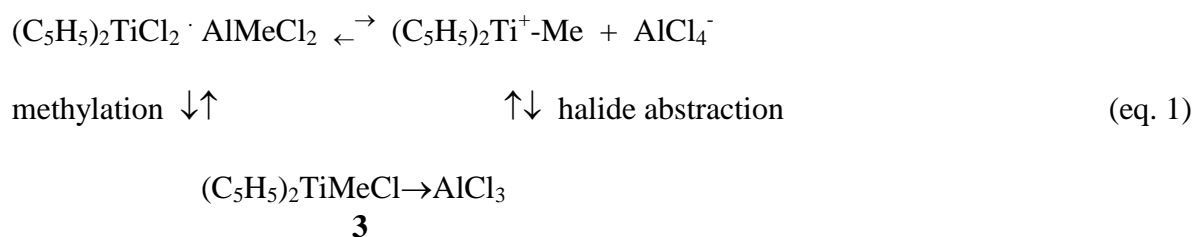
morphology, the metallocene systems have to be heterogenized on support materials.^{4,16,17} (In connection with the heterogenation of metallocenes we note that activated zirconocenes were recently intercalated in silicates and tested for olefin polymerization.¹⁸) Other descriptive names found in the literature for the zirconocene catalysts are "molecular-defined" or after the names of the founders and long-time principal investigators "*Kaminsky-Brintzinger*" systems.

The impact of "metallocene catalysts" extends beyond simple olefin polymerization. It has opened the doors to new classes of polyolefins inaccessible by classical Ziegler-Natta polymerization. It has advanced the development of chiral metallocenes. It is promoting the interest to explore further possible applications of metallocenes in general and it is encouraging the search for other single-site catalysts in place of heterogeneous industrial systems. We would like to close this introduction by noting that further information, additional or different views on the various aspects of metallocene catalysis for the polymerization of olefins can be found in the following references^{19,20,21,22,23,24}.

2. Historical Development

Metallocene catalysts for the polymerization of ethene are almost as old as Ziegler-Natta catalysis itself. In 1957, *Natta, Pino et al.*²⁵ and independently *Breslow and Newburg*²⁶ reported on a soluble, crystalline and isolable²⁷ complex from $(C_5H_5)_2TiCl_2$ and $AlEt_3$ which was polymerization active towards ethene but much slower than a comparative heterogeneous Ziegler catalyst, e.g. $TiCl_4/AlEt_3$. *Breslow and Newburg* did, however, note that traces of oxygen in the monomer increased the catalyst activity. $(C_5H_5)_2TiCl_2$ alone is completely inactive towards ethene polymerization. *Natta et al.* recognized the value of these "bimetal complexes" for the study of the heterogeneous Ziegler catalysts.²⁸ In the following two decades, $(C_5H_5)_2TiCl_2$ with different alkylaluminium halide cocatalysts ($AlMe_2Cl$, $AlEt_2Cl$, $AlEtCl_2$), because of its well defined character, and the low polymerization activity, was used as a model

system to develop an understanding of the classical Ziegler catalysis. Important ideas for the elementary processes, the mechanism of Ziegler-type polymerization reactions were derived therefrom, namely having electron deficient compounds as catalysts,²⁹ mechanistic suggestions for Ti alkylation, activation equilibria, Ti-olefin π complex formation, chain growth at titanium and Ti \rightarrow Al chain transfer processes were based on kinetic studies (cf. Scheme 3, section 5).³⁰ The very important suggestion that the catalytic activity of metallocenes is due to the presence of free ions, such as $(C_5H_5)_2Ti^+-Me$ which are formed in some kind of equilibrium reaction, e.g. as in equation 1 via methylation and halide abstraction, was based on electro dialysis studies of the $(C_5H_5)_2TiCl_2/AlMe_2Cl$ system.³¹ We would like to note that these findings by the group of *Dyachkovskii, Shilova and Shilov* were long overlooked or not accepted but later proved ingenious in view of the independent isolation of catalytically active zirconocenium cations with non-coordinating borate anions (see section 4). Confirmation was later also provided by *Eisch et al.* through the observation of an initial insertion of an unsaturated hydrocarbon ($PhC\equiv CSiMe_3$) into the Ti-C bond of the catalytic system derived from $(C_5H_5)_2TiCl_2/AlMeCl_2$. The ion-pair product $[(C_5H_5)_2Ti-C(SiMe_3)=CMePh]^+AlCl_4^-$ was characterized by an X-ray structure, and the cation is schematically depicted in **2**.³² The existence of Ti-Al halide bridged dimetallic species, such as **3** in equation 1, was supported by an X-ray structure of **4**²⁷ and **5**³³ NMR spectral evidence for the generation of equilibrating solvent separated and contact ion pairs in polar halocarbons was found in the interaction of $(C_5H_5)_2Ti(Cl)CH_2SiMe_3$ with $AlCl_3$, giving a system which was active towards ethene polymerization.³⁴



In 1973 and 1975, *Reichert and Meyer*³⁵ and *Long and Breslow*³⁶ noted a strong polymerization rate increasing influence of small amounts of water when added to $(C_5H_5)_2TiEtCl/AlEtCl_2$ and $(C_5H_5)_2TiCl_2/AlMe_2Cl$, respectively. These findings were unusual as water was up till then generally viewed as a catalyst poison for Ziegler systems and perhaps only used to lower the molar mass of polymers.³⁶ Neither of the authors did, however, offer a conclusive explanation for this effect, nor was there a follow-up study by them.

Up to this point chlorine containing titanocene and especially aluminum components were always used and the chlorine content was seen as essential because it was proportional to the polymerization activity. In 1976, *Sinn Kaminsky et al.* could, however, show that a chlorine-free system based on $(C_5H_5)_2TiMe_2$ and $AlMe_3$ became highly active, when water had been added to the aluminum alkyl before reaction with the metallocene.³⁷ The optimum Al to H_2O ratio lay between 2:1 and 5:1 and the formation of alumoxanes (see section) was assumed, no activity was found at a ratio of 1:3 when all three alkyl groups were hydrolyzed. In the same paper, it was also shown that zirconocene complexes could be activated for ethene polymerization. In a follow-up study by the same principal investigators in 1980, methylalumoxane was synthesized separately and employed as an activator for $(C_5H_5)_2ZrMe_2$ to give record high activities of 10^6 g PE/(g Zr · h · bar).³⁸ Lowering the zirconocene concentration and adjusting the Al(MAO):Zr ratio raised the activity further to $3.1 \cdot 10^6$ g PE/(g Zr · h · bar)^{39,40}, the use of $(C_5H_5)_2ZrCl_2$ instead of the zirconocene dimethyl precursor even gave $5 \cdot 10^6$ g PE/(g Zr · h · bar).⁴¹ Although an activity comparison between soluble catalysts in homogeneous solution and carrier supported systems should be judged carefully, on a g PE/g transition metal basis this activity was more than a magnitude higher than those of the best known conventional Ziegler catalyst.⁴² Hence, industrial interest was awakened, but the simple, achiral metallocenes still had a problem: They did not *polymerize* propene (at least not under normal conditions, see

section 7), but gave only atactic polypropene of low molecular weight (oligomers, cf. section 9).^{40,43}

In 1982, *Brintzinger et al.* published the synthesis of the chiral titanocene compounds, *rac*-C₂H₄(Ind)₂TiCl₂ (**6**) and *rac*-C₂H₄(IndH₄)₂TiCl₂ (**7**),⁴⁴ the zirconocene derivatives followed in 1985.⁴⁵ (Scheme 1^{46,47}) The way chosen here (out of other possibilities^{12,48}) to introduce chirality in these metallocenes, is freezing the rotation of the substituted cyclopentadienyl rings by tying them together with a handle, namely the ethanediyl bridge. Using the Latin word for bent handle "ansa", this type of metallocene is also called *ansa*-metallocene.⁴⁹ It may be noted that a C₂ axis of rotation is still present in the enantiomeric forms of **6** and **7** (as well as in many other *ansa*-metallocenes), hence the systems are not asymmetric, only dissymmetric (i.e. lacking mirror symmetry). This is, however, sufficient to induce the existence of enantiomeric forms.⁵⁰ Moreover, we will see in section 7 that the C₂-symmetry of these metallocene catalysts is important in that it provides for the stereoselectivity in propene polymerization. The higher stereoselectivity in transition-metal catalyzed reactions with C₂-symmetrical systems over comparable chiral catalysts with a total lack of symmetry is a general phenomenon and explained by means of a reduced number of possible competing diastereomeric transition states.⁵⁰

This will conclude the historical introduction. How the development took place from here is then presented further in the following separate sections.

3. Methylalumoxane - Characteristics and Function

The development of metallocene catalysis for olefin polymerization is closely tied to the discovery and use of the cocatalyst methylalumoxane (MAO).⁵¹ Alumoxanes in general are understood as species containing an oxygen bridge binding two aluminum atoms - any alkyl, aryl, halide, alkoxy or other group can then be the pendant ligand bonded to the aluminum

atoms. Alumoxanes are an independently studied class of compounds, long known before the interest in the methyl derivative as a cocatalyst for zirconocenes arose.⁵² Alumoxanes are obtained from the controlled hydrolysis of organoaluminum compounds. For methylalumoxane the careful hydrolysis of trimethylaluminum (TMA) by crystal water of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ or $\text{Al}_2(\text{SO}_4)_3 \cdot \sim 14\text{-}18 \text{H}_2\text{O}$ proved to be the most effective laboratory method of obtaining uniform products in high yield.^{52,53,54,55} Technically MAO is made from the direct reaction of water with TMA.

While higher-alkyl alumoxanes are defined monomeric or oligomeric compounds, methylalumoxane still remains a "black box" despite its uniqueness as a cocatalyst. (Other alumoxanes, such as ethyl-, *iso*- or *tert*-butyl-alumoxane, were tried as cocatalysts but did not reach the activity of MAO.^{39,56,57}) Attempts were of course made to elucidate the MAO structure^{55,58}, e.g. with the help of size exclusion chromatography,⁵⁹ NMR,⁶⁰ mass balance and phase separation experiments.⁶¹ The methylalumoxane structure can, however, only be postulated as being a mixture of linear (**8**) or cyclic (**9**) oligomers of MeAlO units, and is most often represented as such. Cluster structures capable of enclathrating a chloride ion or a metallocene in a host-guest complex (**10**) have been suggested as well.^{62,63}

From its synthesis MAO contains residual trimethylaluminum (about 5% in commercial MAO-toluene solutions is given in company certificates, while other studies suggest up to 25-50%^{60,62,64}), partly free and in part "associated"⁶² to MAO, which is important for the solubility of MAO in aromatic hydrocarbons.⁵⁹ The agreement appears to be that the MAO oligomers are fluxional molecules with a dynamic equilibrium among them, which changes their size and structure.^{16,62} The average molecular weight depends on the preparative conditions⁵⁵ (about 900-1100 g/mol for the commercial 10 wt.-% -toluene solutions). Toluene solutions of MAO obviously "age" within several weeks time (especially when the flask is opened more often

under inert gas, so that free TMA evaporates) leading to gel formation and a change (usually an increase) in their cocatalytic activity when used in polymerization catalysis.⁶⁵

The full cocatalytic functionality of MAO towards zirconocenes is also unknown.⁵⁷ An NMR⁶⁶ and a combined IR/NMR study on zirconocene dichloride/MAO systems⁶⁷ or an X-ray structure of a neutral dimethylzirconocene/aluminoxane adduct $\{(C_5H_5)_2ZrMe(\mu-OAlMe_2)\}_2$ ⁶⁸ did not shed much light on this question. Aside from alkylating the metallocene dihalide, abstracting a chloride or alkide with the formation of a $[Cp_2ZrMe]^+$ cation and being a scavenger for impurities, the cocatalytic function of MAO is probably best described as establishing a stabilizing environment for the metallocene cation or cation-anion pair in the form of a host-guest or "crown-alumoxane" complex.⁶⁹ This may appear akin to enzymatic catalysis where the organic hull of the enzyme protects its active center. The formulation of metallocene cations as the active species is based on the work of *Dyachkovskii et al.* noted above³¹ and on the synthesis of isolable and olefin-polymerization active cations by independent routes (cf. section 4). The identity of the polymers obtained with the ionic zirconocenium-borate catalysts and with zirconocene/MAO systems was also taken as an indication that essentially the same cationic $[Cp_2ZrMe]^+$ species are the active form in the latter. Furthermore, X-ray photoelectron spectroscopy studies on Cp_2ZrR_2/MAO ($R = Cl, Me$) also suggested the formation of cationic species.⁷⁰ While in the heterogeneous Ziegler-Natta systems Ti(III) constitutes the active species, reduction of $(C_5H_5)_2ZrCl_2$ with the formation of Zr(III) does occur with MAO but is negligible during the first few hours, according to an EPR-study.⁷¹

It has been found that very high ratios of MAO to metallocene are required to achieve a good polymerization activity. The use of UV-Vis spectroscopy was suggested to follow the activation with Al/Zr and catalyst stability over time.⁷² Furthermore, the activity of the Cp_2ZrCl_2/MAO catalyst often seems to increase "indefinitely" with the increase of the Al:Zr

ratio.^{39,40,43,53} This effect is usually discussed on the assumption of an equilibrium between an inactive metallocene precursor and its catalytically active form (equation 2).^{73,74}



With the *ansa*-metallocenes $\text{C}_2\text{H}_4(\text{IndH}_4)_2\text{ZrCl}_2$,⁶⁹ $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{Flu})\text{ZrCl}_2$, and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ ⁷⁵ a maximum activity for molar Al/Zr \approx 3500, 1300, and 10900, respectively, was reported in propene polymerization and also in ethene polymerization for the latter two with Al/Zr \approx 5100 and 26600, respectively. For propene polymerization it was also found that the catalyst activities and polymer molecular masses depended upon the MAO concentration, whereas zirconocene concentration and the Al/Zr molar ratio were less significant. A competition between MAO and propene for the vacant coordination sites was invoked to explain the adverse effect on the catalyst activity. Optimum performance with the *rac*- $\text{Me}_2\text{Si}(2\text{-Me-benz[e]indenyl})\text{ZrCl}_2$ complex in terms of activity and molecular mass was obtained at an MAO concentration with $[\text{Al}] = 5 \text{ mmol/l}$.⁷⁶

The activation equilibrium sketched in equation 2 is just a simplified version of a most likely much more complicated kinetic scheme with a combination of at least two dynamic equilibria between temporarily inactive (dormant), active, and deactivated zirconocene dimers.⁷⁷ The analysis of data from the ethene polymerization with $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$ and temperature, zirconocene and MAO concentration as variables suggested the presence of two kinds of active species. One kind of species is produced from the other via a pseudo-first-order reaction.⁷⁸ Similarly two successive dynamic equilibria were found in the system $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{propyl})\text{Cl}/\text{AlEtCl}_2$, where a second equilibrium, which lies mostly on the "left side", leads to the active complex and requires a large aluminum excess to be shifted fully to the right.⁷⁴ In line with the formation of ion pairs, the solvent polarity has a considerable effect not

only on the activity (increasing with polarity) but also on polymer molar mass and tacticity (for propene).⁷⁹

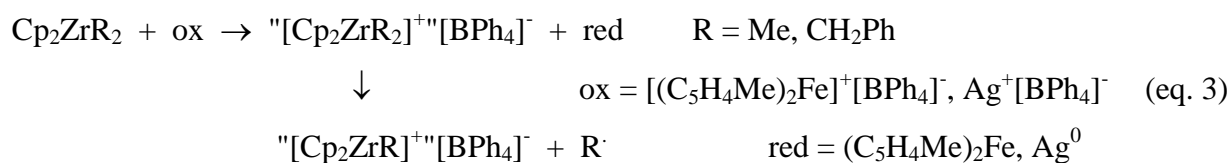
Many zirconocene systems described in the literature require Al:Zr ratios on the order of 1000:1 to 10 000:1 to achieve a reasonable activity. The necessary Al:Zr ratio also depends on the zirconocene concentration. At very small zirconium concentration the MAO content has to be increased overproportionally to prevent dissociation of the active complex upon dilution according to the law of mass action.^{73,80,81} For the record high activities reported by *Kaminsky et al.*^{38,41} extremely high Al:Zr ratios of 150 000:1 or even 500 000:1 were employed for the very small metallocene concentrations of 10^{-7} and 10^{-8} mol/l, respectively. Economically such high excess ratios of the expensive MAO are very unfavorable because it makes the cocatalyst *the* actual cost factor in metallocene/MAO-catalysis and investigations were carried out to reduce the ratio MAO/metallocene. Apparently, up to 90% of the MAO can be replaced by TMA without significant loss in polymerization activity towards ethene.⁵³ Necessary reactivation reactions from bimetallic deactivation processes and equilibria (cf. section 5) are apparently responsible for the high MAO excess, appropriate substitution at the cyclopentadienyl or indenyl ligands can decrease the probability for deactivation resulting in less excess of MAO. The MAO/metallocene ratio can also be reduced by supporting the metallocene on a solid surface, e.g. silica.⁸²

In view of the often high TMA content of MAO, the role of trimethylaluminum in the activation process was also tried to address separately. An NMR study on the reactions, equilibria and polymerizations in $(C_5H_5)_2TiMeCl/AlMe_3$ and $(C_5H_5)_2Ti^{(13)}MeCl/MAO/^{13}C_2H_4$ indicated that MAO is a better alkylating agent and has a greater capacity for producing and stabilizing cation-like complexes, like $[(C_5H_5)_2TiMe^+][Cl-Al(Me)O]_n^-$. At low Al/Zr ratio two types of ion pairs have been detected.⁸³ Zirconocene dichloride and TMA alone were found to be either inactive^{61,83} or to exhibit very low polymerization activity.^{14,60}

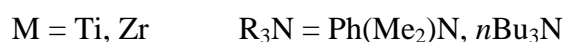
MAO is recently used also in the activation of other, especially zirconium nitrogen and oxygen coordination complexes for olefin polymerization.⁸⁴ We close this section by noting that there are also conflicting reports as to actual role of MAO in metallocene catalysis (e.g.⁶⁰) and because of the complexity or ill-definition of this cocatalytic system other activators or MAO substitutes were and are still sought (*vide infra*). An early yet not economically viable example presented the system $\text{AlMe}_3\text{-AlMe}_2\text{F}$ in CH_2Cl_2 demonstrated for the activation of $(\text{C}_5\text{H}_5)_2\text{TiPh}_2$.⁸⁵ Until today the only alternative to MAO are non-coordinating borate counterions. These will be the topic of the next chapter.

4. The Borane Activators or Cationic Catalysts and other Cocatalyst-free Systems

In 1986, *Jordan et al.* first opened the possibility to synthesize and isolate cationic metallocene complexes of group IV and he showed that they polymerize ethene in the absence of an aluminum cocatalyst.^{86,87} One-electron oxidants were used to generate the zirconocenium cations (equation 3), which could then be trapped in the presence of labile ligands L (equation 4). In CH_2Cl_2 solution, the THF partly dissociates from the complex $[\text{Cp}_2\text{ZrR}(\text{THF})]^+[\text{BPh}_4]^-$ which catalyzed ethene polymerization in low yield. The THF ligand functions as an inhibitor since no activity is observed in tetrahydrofuran solution and the transient intermediate $[\text{Cp}_2\text{ZrR}]^+[\text{BPh}_4]^-$ when generated in CH_2Cl_2 in the presence of ethene gave a much more rapid polymerization catalyst ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$).

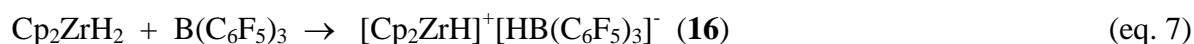
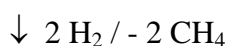


An alternative access to cationic group IV metallocenes was developed by *Hlatky, Turner and Bochmann et al.* through the protonolysis of metal-alkyl bonds with tertiary ammonium-tetraphenylborate (equation 5).^{88,89} This route leads to ionic, base-free (aside from the amine) zirconocene catalysts, which are active even in solvents such as toluene or hexane. With the amine still present, the formation of weakly bound amine complexes may be assumed (**11**, scheme 2).⁸⁹

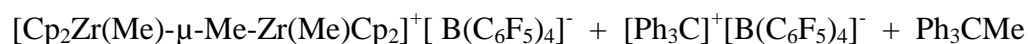
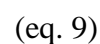


The reaction in equation 5 or the cation-anion interaction can become more complicated, however, as from the reaction of $(\text{C}_5\text{Me}_5)_2\text{ZrMe}_2$ with $[n\text{Bu}_3\text{NH}][\text{B}(p\text{-C}_6\text{H}_4\text{Et})_4]$ in toluene, the zwitterionic, yet polymerization-active compound **12** (scheme 2) was obtained. In **12** one of the phenyl rings is metallated in the meta position, probably by an electrophilic attack of the intermediate $[(\text{C}_5\text{Me}_5)_2\text{ZrMe}]^+$ cation and CH_4 elimination.⁸⁸ Low-temperature proton NMR investigations could prove a fluctuating η^2 coordination of a phenyl ring from BPh_4^- to the cationic zirconium center (**13**, scheme 2).⁹⁰ Hence, aside from irreversible deactivation reactions, solutions of the cationic metallocenes obtained according to equation 5 contain several species in equilibrium (scheme 2)^{23b} which compete with the olefin complex (**14**, scheme 2). Subsequently, the polymerization activity was still low when compared to MAO-activated systems. To further enhance the activity of cationic metallocene catalysts it is necessary to increase the concentration of the actual polymerization active complex **14** (scheme 2). If the equilibrium between **13** and **14**, i.e. the cation-anion interaction and the anion displacement by the olefin, was of special importance then even weaker coordinating anions had to be introduced.⁹⁰

To achieve this, perfluorinated arylboranes were used. *Marks et al.* employed tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, and with Cp_2ZrMe_2 obtained a crystallographically characterizable, active polymerization catalyst.⁹¹ In a side-product free reaction, the borane abstracts a methyl group from the metallocene (equation 6) to give in the solid state a weakly coordinated cation-anion pair with a non-linear $Zr(\mu-Me)B$ bridge (**15**). The same feature was observed in the structure of $\{C_5H_3-1,3-(SiMe_3)_2\}_2ZrMe(\mu-Me)B(C_6F_5)_3$.⁹² Perhaps a similar interaction is present in zirconocene/MAO systems. Hydrogenolysis of **15** or hydride abstraction from Cp_2ZrH_2 by $B(C_6F_5)_3$ gives a hydride complex **16** (equation 7), where the anion is weakly coordinated by $Zr \cdots F$ contacts.⁹³ The perfluorated borate anions presented here are also referred to as "non-coordinating" anions.



To use the tetraarylborate anion and at the same time avoid the presence of amines, triphenylcarbenium (trityl) -borate salts can be reacted with Cp_2ZrMe_2 ; aryl is usually pentafluorophenyl (equation 8).⁹⁴



The counterion, e.g. $[B(C_6F_5)_4]^-$ versus $[MeB(C_6F_5)_3]^-$, has an effect on the activity and stereoselectivity, when chiral catalysts are used.⁹⁵ The sole description of the zirconocene methyl cations as monomeric species may, however, be too simple. It was shown that dimeric complexes initially form at low temperature when Cp_2ZrMe_2 is reacted with $[Ph_3C]^+[B(C_6F_5)_4]^-$

(equation 9). The stability of the dimer and its tendency to further react with the trityl borate to give the monomeric cation depends on the nature of the Cp-ligand; with bridged bis(indenyl) ligands the reaction proceeds only above 0 °C.⁹⁶ A dimeric complex, as described in equation 9, could recently be crystallographically characterized (**17**) by using the bulky tris(perfluorobiphenylborane) (**18**) as an abstracting agent. The reduced coordinative tendencies of the resulting bulky borate [Me-**18**]⁻ stabilize the dimer, even with excess borane and long reaction times.⁹⁷ The very weak ion-pairing behavior of this bulky borate versus [Me-B(C₆F₅)₃]⁻ lead to a significant activity enhancement with constrained geometry ("Dow") catalysts towards ethene and ethene/hexene copolymerization.⁹⁷

In **15** and **16** the cation-anion contacts are apparently this weak that the "non-coordinating" anion can be easily displaced by the olefin. Quantitative thermodynamic and kinetic parameters for ion pair formation, dissociation and reorganization in [(C₅H₃-1,2-Me₂)₂MMe]⁺[MeB(C₆F₅)₃]₃⁻ complexes (M = Zr, Hf)⁹⁸ and other metallocenium ions⁹⁹ in various solvents are available. The activity of these ionic, base-free catalysts is comparable or even surpasses that of zirconocene/MAO systems, yet in the absence of scavenging agents, the cationic catalyst is not very long lived. Polymerization times given are in the range of minutes.^{94,100} Thus, in applications of the borate-activated catalysts, higher aluminum alkyls are favorably added to act as purifying agents and thereby enhance the observed activity.^{95,101} Except trimethylaluminum is not suitable as a scavenger here, because of inactive heterodinuclear dimers which are formed in equilibrium with the monomeric cations (equation 10).⁹⁶ With AlEt₃ related heterodinuclear dimers form but dissociate more readily so that polymerization activities increase in the order Me < Et.¹⁰²



Addition of $B(C_6F_5)_3$ to zirconocene butadiene yields a zirconium-boron betain complex (**19**, equation 11)¹⁰³ which allowed the observation of the first insertion step at a single-site catalyst. The primary insertion products (**20**) for both ethene and propene (equation 12) are stable at $-50\text{ }^\circ\text{C}$ and could be observed by NMR spectroscopy. The complexes **20** are still active polymerization catalysts forming polyethene and -propene upon temperature increase in the presence of excess monomer.¹⁰⁴

Ion cyclotron resonance mass spectrometry was used to study the reaction rates of five different bridged and unbridged $[Cp_2Zr-CH_3]^+$ cations with H_2 and C_2H_4 . After insertion of ethene the resulting propyl complex dehydrogenates to give the final product, presumably an η^3 -allyl complex. For the reaction $[Cp_2Zr-CH_3]^+ + C_2H_4 \rightarrow [Cp_2Zr-C_3H_5]^+ + H_2$ the rates decrease with increasing steric demand of the Cp_2 -ligands in the order $Me_2Si(C_5H_4)_2 > (C_5H_5)_2 > (C_5H_5)(Ind) > (Ind)_2 \gg (Flu)_2$.¹⁰⁵

Group III and Lanthanoide Metallocene Catalysts: Neutral group III (Sc, Y, La) and lanthanoide metallocene complexes of the general type Cp_2MR ¹⁰⁶ and $[Cp_2MH]_2$,¹⁰⁷ which in their monomeric form are iso-d-electronic (d^0 , not counting the f-electrons) with $[Cp_2ZrR]^+$, are also capable of polymerizing ethene in the absence of a cocatalyst and show the same mechanistic features (see below), such as olefin insertion, β -H elimination and M-R bond hydrogenolysis as the zirconocene catalysts. New studies in this direction also involve divalent samarocene, Cp_2Sm ¹⁰⁸ as well as *ansa*- $Cp_2Sm(THF)_2$ ¹⁰⁹. A single-component chiral organoyttrium *ansa*-metallocene catalyst $[Me_2Si(C_5H_2-2-SiMe_3-4-tBu)_2YH]_2$ was found to slowly polymerize propene (97% isotactic), 1-butene, 1-pentene, and 1-hexene.¹¹⁰ The ring-opening Ziegler polymerization of methylenecyclopropane (cf. equation 19) with $\{(C_5Me_5)_2LnH\}_2$ ($Ln = Sm, Lu$) gave exo-methylene functionalized polyethenes.¹¹¹ Group III and lanthanoide metallocenes, e.g. $(C_5Me_5)_2LnMe(THF)$ ($Ln = Y, Sm, Yb$), $\{(C_5Me_5)_2SmH\}_2$,

and $(C_5H_4Me)_2Yb(DME)$, are also used as initiators for the polymerization of polar monomers such as alkyl acrylates to give high molecular weight polymers with extremely narrow molecular mass distribution.¹¹²

5. General Mechanism of Chain Growth, Chain Transfer and Deactivation

Homogeneous group IV metallocenes polymerization catalysts were initially investigated to understand the long-debated mechanism of Ziegler-Natta catalysis (see section 2). The essential features for the insertion polymerization, derived therefrom, are collected in Scheme 3. For the insertion of an olefin into a transition metal alkyl bond in Ziegler-Natta polymerization (part **b** in Scheme 3), three basic mechanisms have been suggested, each being supported by experimental evidence: (i) the direct insertion mechanism, proposed by *Cossee and Arlman*,¹¹³ involving a loosely coordinated four-centre transition state (Scheme 4); (ii) the metathesis mechanism, proposed by *Green and Rooney*,¹¹⁴ in which an α -hydrogen transfer from the end of the polymer chain and formation of a metal carbene/alkylidene precede the formation of a metallacyclobutane complex (Scheme 5) and (iii) the "modified Green-Rooney mechanism" (see below).

α -Agostic Interactions and the Modified Green-Rooney Mechanism:¹¹⁵ Intermediate between the Cossee-Arlman and the Green-Rooney mechanism (see above), the "modified Green-Rooney mechanism" has been suggested (by *Brookhart and Green*) for olefin insertion into a transition metal alkyl bond.¹¹⁶ There, an α -agostic C-H interaction in a transition state was proposed to assist the insertion of an olefin (Scheme 6). With respect to the last mechanism, a number of experiments have been designed to explore the suggested role of an α -agostic intermediate in the olefin insertion reaction. Thus, while the product of an induced cyclization in racemic 1- d_1 -5-hexenyl- and heptenylchlorotitanocene (equation 13) argued against an α -CH activation,¹¹⁷ the hydrocyclization of *trans,trans*-1,6- d_2 -1,5-hexadiene by a

scandocene hydride, $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Sc}(\text{PMe}_3)\text{H}$ (equation 14)¹¹⁸ as well as the hydrodimerization of (*E*)- or (*Z*)-1-deuterio-1-hexene by achiral zirconocene dichloride/MAO (equation 15)¹¹⁹ gave results, which were judged to provide experimental evidence for an α -agostic transition state (modified Green-Rooney mechanism) in metal catalyzed olefin polymerizations. The *cis:trans* or *erythro:threo* ratio differing from unity in equation 14 or 15, respectively, is seen to stem from an H/D-isotope effect, whose basis is the expected preference of H over D in an α -agostic interaction as shown in Figure 2 for the transition states. In $[(\text{C}_5\text{Me}_5)_2\text{Hf}(\text{CH}_2\text{CHMe}_2)(\text{PMe}_3)]^+$ NMR data established the distortion of the isobutyl group by an α -agostic interaction.¹²⁰ α -Hydrogen and to a lesser extent also β -hydrogen participation was demonstrated in the MgX_2 and MAO promoted intramolecular olefin insertion (cyclization of alkenyl ligands) of Cp_2TiClR complexes.¹²¹

From a study on polymerizations of deuterium labeled (*E*)- and (*Z*)-propene-1-*d* by chiral *ansa*-zirconocene catalysts, direct experimental evidence has now been obtained for the role of α -agostic interactions in the formation of isotactic polypropene. Polymerizing either (*E*)- or (*Z*)-propene-1-*d* with *rac*- $\text{C}_2\text{H}_4(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$, *rac*- $\text{Me}_2\text{Si}(\text{C}_5\text{H}_2\text{-}2,4\text{-Me}_2)_2\text{ZrCl}_2/\text{MAO}$ or *rac*- $\text{Me}_2\text{Si}(\text{C}_5\text{H}_2\text{-}2\text{-Me-}4\text{-}t\text{Bu})_2\text{ZrCl}_2/\text{MAO}$ only slightly affects the isotacticities of the polymers formed but significant differences in the mean degree of polymerization, the chain length are evident. Polymers derived from (*E*)-propene-1-*d* have molecular masses which are higher by a factor of 1.3 than those obtained from (*Z*)-propene-1-*d*.¹²²

Some theoretical studies on the mechanism in Ziegler-Natta polymerizations investigated the possibility of agostic interactions. Based on the model system $[\text{Cp}_2\text{Ti-CH}_3]^+ + \text{C}_2\text{H}_4 \rightarrow [\text{Cp}_2\text{Ti-C}_3\text{H}_7]^+$ the direct insertion mechanism (Cossee-Arlman) was found viable without agostic interactions,¹²³ whereas a study on $[\text{Cl}_2\text{Ti-CH}_3]^+ + \text{C}_2\text{H}_4 \rightarrow [\text{Cl}_2\text{Ti-C}_3\text{H}_7]^+$ found strong agostic interactions.¹²⁴ Two Extended Hückel molecular orbital studies conclude that an α -agostic H-Zr contact plays no role in a ground state species but becomes increasingly important

along the reaction coordinate for the C-C bond-forming insertion reaction. As the Zr-C_{alkyl} bond weakens and the zirconium center becomes more electron deficient, the α -agostic interaction stabilizes (lowers the energy of) the transition state by relieving part of the electron deficiency of the 14-valence electron species.¹²⁵

Theoretical Considerations on Olefin Coordination and Insertion: The aforementioned ligand abstraction in a metallocene derivative Cp₂MR₂ creates the space and metal orbital necessary for the σ -interaction with the incoming olefin (Figure 3a).¹²⁶ Because there are no d-electrons available for π -backbonding in a d⁰ system into the empty π^* -orbitals of the olefin (Figure 3b), the metal-olefin interaction is not stabilized and remains weak. The cis-positioned alkyl ligand (chain end) can then be transferred to the olefin or in other words the olefin inserts into the metal-alkyl bond. This dynamic olefin insertion process has been studied theoretically several times on various levels of sophistication, such as density functional theory¹²⁷ or by *ab initio* methods.^{123,128} Figure 4 illustrates the ethene insertion into the Zr-Me bond of [Cp₂ZrMe]⁺ according to MO-calculations. Table 1 summarizes the energetics calculated by different methods and various levels of theory for the binding of ethene to the positively charged [Cp₂MMe]⁺ cation (M = Ti, Zr) forming the π -complex (**21**), for the transition state (**22**) and for the γ -agostic primary product (**23**, cf. Figure 4)

Table 1. Energetics of the ethene insertion in the Cp₂MMe⁺-C₂H₄ system on various levels of theory^a

Cp ₂ MMe ⁺ cation	method/level of theory [Ref.] ^b	π -complex	transition state	γ -agostic product
(C ₅ H ₅) ₂ ZrMe ⁺	non-local DF ^c [127b]	-96	-93	-128
(C ₅ H ₅) ₂ TiMe ⁺	SCF/SCF ^{d,e} [128c]	-22.3	+52.2	-90.9
(C ₅ H ₅) ₂ TiMe ⁺	MP2/SCF ^{d,f} [128c]	-99.0	-121.7	-135.2
(C ₅ H ₅) ₂ TiMe ⁺	MP2/MP2 ^{d,g} [128c]	not existent ^h	not existent ^h	-188.9 ⁱ

$(C_5H_5)_2TiMe^+$	local DF ^a [128c]	not existent ^h	not existent ^h	-195.1 ⁱ
$H_2Si(C_5H_5)_2ZrMe^+$	RHF/RHF ^j [128d]	-80	-10	-100
$H_2Si(C_5H_5)_2ZrMe^+$	MP2/RHF ^{dj} [128d]	-140	-115	-161

^a Energies given relative to Cp_2MMe^+ and C_2H_4 in kJ/mol - ^b for further details on optimized, basis sets etc. see the original literature - ^cDF = density functional - ^d SCF = self-consistent field, MP2 = second-order Møller-Plesset perturbation - ^e SCF energy at the SCF equilibrium geometry - ^f MP2 energy at the SCF equilibrium geometry - ^g MP2 energy at the MP2 equilibrium geometry - ^h does not exist on the correlated level - ⁱ additional α - (higher energy) and β -agostic products (lower energy) besides the γ -agostic product have been calculated on the correlated level. - ^j restricted Hartree-Fock (RHF) energy and MP2 energy at RHF geometry, respectively

Models for $Cp_2Zr(R)(olefin)^+$: Olefin complexes of the type $Cp_2Zr(R)(olefin)^+$ are assumed as intermediates in olefin polymerization processes with metallocene catalysts, but they have never been observed. In view of the weak zirconium-olefin interaction because of lack of $d-\pi^*$ backbonding in the d^0 system (cf. Figure 3) and the ready possibility for insertion into the Zr-R bond the elusive nature of such an olefin complex is understandable. On the other hand, the characterization of $Cp_2Zr(R)(olefin)^+$ would help in the understanding how a such cationic catalyst coordinates the olefin and activates it for the migratory insertion. Attempts to design model complexes for $Cp_2Zr(R)(olefin)^+$ lead to the synthesis and structural characterization of **24**.¹²⁹ Group-IV metallocene ethene complexes of the type $Cp_2M(RHC=CHR)PMe_3$ ($M = Zr, Hf$; $R = H, Ph$) are known and structurally or spectroscopically characterized.¹³⁰ Also, the structure of an ethylene-bridged zirconocene complex, $\{(C_5H_5)_2ZrMe\}_2(\mu-\eta^2,\eta^2-C_2H_4)$, with ethene side-on coordinated to each metal center, is available.¹³¹ In each case the olefin is lying in the plane bisecting the angle spanned by the two cyclopentadienyl ring planes.

Regiospecificity in α -Olefin Insertion: The mechanical properties of different polypropenes (PP) and other poly- α -olefins strongly depend on their microstructure, which is determined by the regio- and stereospecificity (tacticity). Regiospecificity concerns which end of the α -olefinic double bond is linked to the metal atom of the catalyst and which end to the growing chain: Scheme 7 illustrates that if position 1 (the CH₂-end) of propene is connected to the metal center and position 2 (the CHMe-unit) to the chain end, then the so-called "1-2" (also 1,2- or primary) insertion or addition results. This is the normal type of insertion preferred by the classical Ziegler-Natta¹³² and metallocene catalysts. When position 2 of the olefin is linked to the metal center a "2-1" (also 2,1- or secondary) insertion follows. Consecutive regioregular insertions result in a head-to-tail enchainment. Regioirregularities such as a 2-1-addition in a series of 1-2-insertion (and vice-versa) than leads head-to-head and tail-to-tail structures if the secondary alkyl ligand does not isomerize to a primary ligand before the next insertion to what then becomes a 1-3 insertion. At higher temperature, isomerization or 1-3 insertion becomes more dominant and can replace all original 2-1 insertions.¹³³ A 2-1 insertion represents a steric hindrance to further chain growth, often leads to a β -hydride elimination or can be overcome via a β -hydride shift initiated isomerization leading to a 1-3 insertion.¹³⁴ (Another way to overcome this is to incorporate ethene as a comonomer to activate the catalysts sites blocked by a 2-1 insertion.¹³³)

The polyolefin molecular mass is substantially affected by a variation in transition metal concentration such that a decrease in zirconium concentration gives rise to a large increase in molar mass.^{39,40,81} Two possible explanations are discussed for this not fully understood phenomenon:²¹ (a) a dilution effect favoring the active complex form over the inactive precursor or dormant species in equilibrium (cf. equation 2 and 16) and hence the rate of chain propagation over that of chain termination. It is thereby assumed that chain terminations arise

predominantly from dormant, i.e. temporarily inactive zirconocene species. (b) A bimolecular chain-transfer mechanism involving the active complex and a second (active or inactive) zirconocene species is proposed by *Kaminsky et al.*^{39,40} such that a decrease in zirconocene concentration would then reduce the rate of the termination reaction.

Chain Transfer Processes, β -Agostic Interactions, β -Hydride, β -Methyl Elimination: The four principle chain transfer processes have already been shown in Scheme 3 with ethene as a monomer. For propene, a β -methyl elimination as a fifth transfer process (see below) and the type of end group formed deserves an additional attention (Scheme 8). Two main chain types of chain transfer processes have been observed with (chiral) metallocene catalysts: chain transfer by β -H elimination to the metal center, leading to an olefinic end group, and chain transfer to the aluminum cocatalyst, giving a saturated end group after hydrolytic workup. In low molecular mass polypropenes, an end group analysis by ^1H and ^{13}C NMR spectroscopy²³⁸ can be used to determine the type of chain transfer process. Chain transfer by β -H elimination to the metal center can take place after a primary or secondary insertion and gives metal-hydride species which serve then as a new starting point for chain start, giving rise to n-propyl start groups (Scheme 8a). This monomolecular type of chain transfer is zero order in monomer concentration. Concerning the last inserted monomer unit, a preceding primary insertion leads to a vinylidene end group while a monomolecular hydrogen transfer after a secondary insertion produces vinyl and 2-butenyl end groups (Scheme 8b).¹⁹⁷

Furthermore, chain transfer via β -H elimination can also be bimolecular, thereby involving hydride transfer to monomer (Scheme 8c and d) so that the reaction becomes first order in monomer concentration. After a 1-2 insertion this bimolecular process will produce identical end groups to the monomolecular hydrogen transfer. In case of a preceding secondary insertion, on the other hand, clearly a methylene hydride transfer to the monomer occurs, thus,

giving 2-butenyl end groups. Elimination from a methyl hydrogen is not observed with bis(indenyl)-catalysts and unlikely due to steric hindrance as the growing chain would be forced towards one of the six-membered indenyl rings. The ratio between the rates of H transfer to metal and to monomer can be estimated, at a given polymerization temperature, by evaluating the polymer molecular mass dependence on propene concentration.¹⁹⁷

An additional transfer mechanism possible in propene polymerization is chain transfer via β -CH₃ elimination (Scheme 9). Oligomeric products obtained with the special decamethylmetallocene catalyst system (C₅Me₅)₂MCl₂/MAO (M = Zr, Hf)²³⁸ or [(C₅Me₅)₂ZrMe]⁺[MeB(C₆F₅)₃]⁻⁹¹ were found by NMR to be mainly vinyl- and isobutyl-terminated. The vinyl to vinylidene (from β -H transfer) ratio was 92/8 for M = Zr and 98/2 for Hf. The isobutyl (chain start) group structure is produced by monomer insertion into the M-CH₃ bond (Scheme 9). The β -alkyl elimination appears to be limited to alkyl = methyl, with 1-butene as a monomer no β -ethyl elimination was detected.²³⁸ The preference for β -methyl versus β -hydrogen elimination with (C₅Me₅)₂M catalysts can be attributed to a lower steric hindrance in the transition state **25** versus **26**, where the β -Me group or β -H have to be oriented towards the metal in the bisecting plane. The additional nonbonded interactions indicated in **26** disfavor this transition state and subsequently β -hydrogen transfer to the metal.²³⁸

The role of β -hydrogen transfer in the polymerization with metallocene catalysts has been studied theoretically by density functional and molecular mechanics method.¹³⁵ As a model for β -agostic interactions which may be present in the Cp₂ZrR⁺ and Cp₂M(R)(olefin)⁺ ions, the X-ray structure of (C₅H₄Me)₂Zr(PMe₃)CH₂CH₃⁺ is suggested, which revealed an H ^{β} -Zr contact of 2.16 Å.¹³⁶

In the case of α -olefins, a regioirregular or 2-1 insertion (see above, Scheme 7) leaves the active site in a deactivated state for further olefin insertion and is the preferred mode for chain

termination by β -hydride elimination. One way to overcome the steric hindrance to further chain growth built up by a 2-1 insertion is a β -hydride shift initiated Zr-chain isomerization which leads to a 1-3-insertion.¹³³

Deactivation: The activation of Cp_2ZrCl_2 by MAO involves a very fast reaction yielding the catalytically active sites. From there, the catalyst activity decays depending on temperature and catalyst characteristics. For the well investigated system $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$ there is a very rapid initial activity decay above 40 °C during the first few minutes followed by a second slow deactivation, at 0 °C the activity slowly decreases over hours. It is suggested that the catalytically active complexes C^* are deactivated in a two-step deactivation process by a reversible followed by an irreversible process to form inactive species I_1 and I_2 (equation 16).^{77b}



At low temperature k_2 is very small and in an approximation there is only reversible deactivation. Both deactivation processes are second order with respect to the catalytically active sites. The species I_1 which can recover and again take part in propene polymerization is also called "dormant". The kinetic schemes did not permit the identification of the actual reaction mechanism.⁷⁷ Reduction of Zr(IV) to Zr(III) may play a role in the irreversible deactivation, since this process is accentuated in the presence of ethene, compared to ethene-free $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ -system.⁷¹

Kaminsky et al. showed that methane develops when metallocenes are reacted with MAO¹³⁷ or other aluminum alkyls,⁴⁰ due to α -hydrogen transfer from a methyl group and with the formation of an intermittingly catalytically inactive $\text{M-CH}_2\text{-Al}$ complex. The Al/Zr ratio, temperature and type of catalyst determine the rate of gas evolution. Excess MAO than reactivates the inactive $\text{M-CH}_2\text{-Al}$ structures via ligand exchange. A similar α -hydrogen

elimination with formation of methane and still slightly active Zr- μ -CH₂-Zr complexes was demonstrated by *Bochmann et al.* in cationic zirconium alkyl complexes.¹³⁸

When one cyclopentadienyl ring is lost, as can be the case in non-*ansa*-metallocenes at elevated temperature under polymerization conditions, the resulting mono-cyclopentadienyl or half-sandwich complexes can still be active ethene polymerization catalysts.¹³⁹

The Problem of Comparing Activities, "A Caveat": Activity in the context of olefin polymerizations with metallocene/MAO systems should always be judged as an "apparent activity", since differences in dynamic activation equilibria (equation 2 and 16) of different complexes with MAO cannot be taken into account.⁷⁷ The same activity of two complexes does not necessarily imply that both have the same concentration of active species even if all conditions are identical. There does not seem to be a method available to determine the active center concentration. Radiotagging by quenching a polymerization with tritiated methanol, CH₃O³H, which is occasionally advocated^{53,140} cannot exclude the dormant or inactive sites if they carry an organo-group or hydrogen atom.

In the literature of metallocene catalysis often activity data for related complexes is taken from the sources of other workers. Such a comparison should be judged very carefully because of the unavoidably different polymerization conditions. The large number of obvious and less obvious parameters often renders such comparisons rather dubious. Obvious parameters which affect the activity are e.g. temperature, Al:Zr concentration, pressure, and solvent, less obvious are probably zirconocene concentration, quality of MAO (degree of oligomerization, age, TMA content)⁵⁵ and the monomer purity, pre-activation times between the zirconocene and MAO, reactor preparation, stirrer frequency etc. Carefully carried out comparative polymerization runs where all variable except for the metallocene catalyst were kept the same are very seldom to

find, especially if they involve more than two or three different compounds.^{80,81,152} Also, if working catalytically with very small catalyst concentrations meaningful activities are obtained as an average from more than one experiment where consistency is observed. Not adhering to this practice and the custom to collect activity data from the literature for comparison may be the source of many of the conflicting ideas²¹ in metallocene catalysis.

Electronic Effects in Olefin Polymerization: The elucidation of ligand effects has been a central piece of work in zirconocene-MAO catalyzed polymerization of α -olefins. Most investigations into ligand effects focus on the influence of the steric environment¹⁴¹ and comparatively few metallocene-polymerization studies have addressed the question how electronic changes in a ligand affect the metal center and its catalytic properties although "electronic" together with steric effects have often been invoked to explain the influence of different cyclopentadienyl ligand substituents¹⁴², however, without any more detailed explanation or proof.

The fundamental problem is to single out the, if any, electronic from the concomitant steric effects.^{80,81} *Piccolrovazzi et al.* employed unbridged indenyl ligands carrying a hydrogen, methyl, methoxy or fluorine ligand in the 4- and 7- position (on the annelated six-membered ring **(27)**).¹⁴³ A similar approach was taken by *Lee et al.* who used bridged and unbridged indenyl ligands on a zirconium center which were similarly substituted at the 4- and 7- or 5- and 6-positions **(28)**.¹⁴⁴ Substituents on the C₆ moiety of these bis(indenyl)zirconium complexes were assumed not to interfere sterically with the incoming monomer, the growing polymer chain or with the insertion reaction at the transition metal center. As a result it was proposed that electron withdrawing groups led to a decrease in catalytic activity and polymer molar mass in the polymerization of ethene and propene, while the effect of electron donors was less clear.¹⁴⁴ Recent results with bis(benz[e]indene)-¹⁴⁵ and bis(4-aryindenyl)zirconium

complexes¹⁴⁶ (see section 7), as well as with *rac*-C₂H₄(Ind)ZrCl₂ having methyl substituents in the 4- and 7-position of the indenyl ring¹⁴⁷ demonstrated, however, a marked steric influence of the substituents on the catalyst propene polymerization behavior. *Möhring and Coville* recently reported a quantification of steric and electronic parameters by the use of cone angles and Hammett functions in the ethene polymerization with (C₅H₄R)₂ZrCl₂-ethylalumoxane catalysts.⁵⁶ Cone angles, NMR-spectroscopic and structural parameters were also used by Möhring et al. to separate the steric and electronic cyclopentadienyl substituent effects of (C₅H₄R)₂TiCl₂ catalysts with Et₃Al₂Cl₃ as an activator in the polymerization of ethene.¹⁴⁸

In accordance with the experimental studies a large number of theoretical calculations have focused on the influence of the steric environment at the metal center (see section 7), however, we are only aware of one theoretical investigation dealing with electronic effects in alkene polymerizations. There, an attempt was made to substantiate the electronic effects deduced with the aforementioned substituted bis(indenyl)zirconium complexes by AM1 calculations on the free ligands.¹⁴⁹

6. Ethene Homopolymerization

In comparison to high-density polyethene (HDPE) from classical Ziegler-Natta catalysts, the so-called metallocene HDPEs are characterized by their low polydispersity and the total absence of branching, which in turn leads to a different rheological behavior.¹⁵⁰

Ethene polymerization studies are often used to investigate basic effects like the influence of catalyst concentration, cocatalyst characteristics and other aluminum alkyls, Al:Zr ratio, temperature, steric effects,¹⁵¹ catalyst formulation on support materials¹⁶ etc. on the catalyst activity and the polymer parameters such as molar mass and molar mass distribution. When comparing different metallocenes ethene may in some cases be better suited as a monomer, since with propene or other α -olefins the stereospecificity of the metallocene strongly affects

the activity.^{152,153,154} The use of ethene and the formation of insoluble polyethene creates, however, problems which one has to be aware of when comparing activities. In an ethene solution polymerization, the C-C bond forming reaction is truly homogeneous only at the very beginning. With the precipitation of polyethene the active complex becomes more and more embedded in the swollen, gel-like polymer matrix, which represents a transfer to the heterogeneous phase,¹⁴ i.e. a heterogeneous active complex form and this leads to a diffusion-controlled reaction. The reaction rate is then controlled by the rate of diffusion of the monomer through the polymer matrix to the enclosed active center^{35,74,155} and can no longer be compared in other terms.^{80,81} In such a diffusion controlled polymerization the activities of different catalyst may then appear very similar, although in reality they are not.

A way out of the problem is to compare the time-activity profiles and to decrease the zirconocene concentration so as to lower the absolute mass of polyethene formed and to mostly remain in the homogeneous reaction regime (Figure 5). This problem of diffusion control adds to the difficulty in comparing polymerization activities from different literature sources. In ethene polymerizations with zirconocene-MAO catalysts the activity under comparable, mostly homogeneous conditions is primarily a function of steric factors. The order of activity follows the order of steric demand. This was demonstrated for a series of methyl-substituted zirconocene pre-catalysts⁸¹ where the steric demand was quantified through the coordination gap aperture¹⁵⁶ (Figure 6).

The polyethene molar mass from metallocene catalysis can be controlled by the metallocene type and concentration, the reaction temperature or by addition of hydrogen through the hydrogenolysis reaction (cf. Scheme 3).^{157,158}

7. Propene Homopolymerization

Propene Microstructures: The three main stereospecific variations, namely isotactic, syndiotactic and atactic PP, and their usual comb-type presentation are depicted in Figure 7. Achiral metallocenes mostly give atactic polypropene which almost always has a low molar mass and is an oily or waxy material (see section 9). Chiral, C_2 -symmetric metallocene/MAO catalysts afford isotactic polypropene. The first such metallocenes used in propene polymerization were the ethanediyl-bridged bis(indenyl)titanium dichloride^{43,44} and bis(tetrahydroindenyl)zirconium dichloride (**6,7**).^{45,159} The titanium compound was, however, a 56/44-mixture of the chiral *racemic* and achiral *meso* isomers (**6a**), hence, the polymer was 63% isotactic and 37% atactic.⁴³ The zirconium derivative, on the other hand, was applied only in its chiral form and subsequently gave isotactic to highly isotactic PP.¹⁵⁹ These first reports on the stereochemical control in polypropene formation appeared in 1984 and 1985, respectively, and they initiated the massive interest by polymer and organometallic chemists in metallocene catalysis, which is still seen now 10 years later. Polypropene is technically the more important polymer over polyethene and changes in the steric ligand situation allow for an unprecedented control of the polymer microstructure. Besides the iso- and atactic mode, other polypropene microstructures, such as iso-block, stereo-block, isotactic-atactic-block, hemiisotactic and especially syndiotactic PP can be obtained, as well, upon ligand modification. Figure 8 gives a correlation between the pre-catalyst and PP-microstructure, illustrating the different degree of stereochemical control. The microstructure can also be greatly affected by temperature. At low enough temperatures, e.g. $-45\text{ }^\circ\text{C}$ for $(C_5H_5)_2TiPh_2$,⁴³ even achiral catalysts are capable of polymerizing propene with stereocontrol, to give e.g. a stereo-block PP (cf. Figure 8).

All of the different forms of homopolypropenes sketched in Figure 8 have different mechanical properties (without the addition of comonomer) ranging from plastic to elastic PP with decreasing stereoregularity. Metallocene catalysts opened up the way to influence the polypropene properties in an understood and controlled way by altering the ligand system of the

metal complexes. This leads to new products with application properties not available with conventional Ziegler-Natta catalysts.⁴

Microstructure Analysis by NMR: Microstructure Analysis of vinyl polymers can be done by ¹³C NMR spectroscopy; for polypropene the methyl region is used. Spectrometers above 200 MHz (¹H, respectively 50 MHz for ¹³C) allow at least for the observation of pentad regions, i.e. can discriminate the chemical shift of a methyl group depending on the relative position of the two methyl neighbors to the right and to the left in the polymer chain. A 150 MHz ¹³C NMR characterization meanwhile allowed for the expansion from the pentad to the nonad level.¹⁶⁰ A special NMR notation is used here for the relative configuration of neighboring centers in vinyl polymers:¹⁶¹ If the pseudo-asymmetric tertiary methin carbon atoms of two neighboring monomer units have the same configuration it is called a *meso* (*m*) diad (**29**), if they are of opposite configuration it is a *racemic* (*r*) diad (**30**). The NMR notation for ideal isotactic PP would then be "... *mmmmmm* ..." for ideal syndiotactic PP "... *rrrrrrr* ...". An example of a spectrum of atactic polypropene and the assignment of the NMR bands to the ten unique steric arrangements of five adjacent monomer units is shown in Figure 9. The spectrum of ideal isotactic or syndiotactic PP would show only one band corresponding to the *mmmm* or *rrrr* pentad, respectively. Interesting are, of course, spectra with more than one and less than nine lines.

The following examples illustrate how ¹³C NMR spectroscopy can be used to draw conclusions on the polymerization, on the structure of the transition state and the mechanism of stereochemical control. An example of a three line NMR spectrum of a polypropene sample is shown in Figure 10. Besides the *mmmm* pentad, the *mmmr* and the *mrmr* (+*rmrr*) pentad are present in a 1:1 ratio. From this the polymer microstructure of a stereo-block PP can be deduced. It is remarkable that such a stereocontrol was achieved with an achiral metallocene

precatalyst. It can be concluded further that the chain-end must be the stereoregulating factor, i.e. the chirality of the methin carbon of the last inserted monomer unit provides stereochemical control during the polymerization. An occasional occurring stereo error (*r* diad) in the insertion results in the new absolute configuration of the last inserted monomer unit which then controls the succeeding enchainment (*m* diads) until the next steric inversion.⁴³

NMR is useful not only in the determination of steric sequence distributions but also in the detection of end groups and structural defects such as regiochemical insertion errors if they are present in amounts greater than 1%.

Stereochemical Control: Stereoregulation in the stereospecific polymerization of α -olefins can either be achieved through interaction between the entering monomer and the growing chain (chain-end control) or through an interaction between the monomer and the metal center and its environment (enantiomorphic-site control) or both.^{132,162} If a chiral metal center provides for the stereocontrol then an occurring stereo error would remain isolated, corrected immediately and result in pentads of the type *mmmr/mrrm/mmrr*, corresponding to an iso-block polypropene, as obtained with the *rac*-C₂H₄(Ind)₂ZrCl₂/MAO system (cf Figure 8).^{132,163,164} An example of a twofold stereodifferentiation was given with the unbridged chiral (C₅H₄CHMePh)₂ZrCl₂/MAO (**31**) and with other conformationally unrestricted (C₅H₄CHR¹R²)₂ZrCl₂/MAO catalysts.¹⁶⁵ The quantitative statistical interpretation of the methyl carbon signal indicates that the isotactic polypropene obtained with **31** consists to 35% of an iso-block PP (enantiomorphic-site control) and to 65% of a stereo-block PP (chain-end control).¹⁶⁴

The polymerization of propene to an isotactic polymer remains a unique example of stereospecificity in organic, nonenzymatic reactions.¹³² How is the stereochemical control

carried out? This will be outlined in the following and with the help of Figure 11. As pointed out above, polymerization of propene (and other α -olefins) takes place (predominantly) by a regioselective 1-2 insertion into the metal-carbon bond. Before insertion, the propene molecule forms a weak π -complex in the 1-2 direction with the transition metal center. This coordination can be done in two prochiral positions (Figure 11a and b). If one of these is energetically favored, then the polymerization will be stereospecific. The spatial arrangement of the bridged metallocene is such that position a (Figure 11) is energetically favored because of less steric interaction with the neighboring six-membered ring of the indenyl system and with the chain end. Insertion then takes place and the next insertion step (c) starts with chain and monomer having exchanged position with each other. For the isotactic polymerization such a chain migration is no prerequisite because even without it the meso stereosequences, i.e. isospecific behavior would result, but the exchange of positions follows from the insertion model presented in Figure 4 and strong evidence is especially provided by the syndiotactic polymerization behavior of the C_s -symmetrical metallocene catalysts (see below).¹⁶⁶

When the insertion occasionally takes place via the other prochiral position (b in Figure 11) a racemic diade is obtained (b→d). If the catalysts shows high isospecific behavior and in case of an enantiomeric site control this stereoerror is immediately corrected (giving a second racemic diade (d→e) and remains isolated. The resulting *mrrm* (*mmrr*) pentad sequences are then typical for enantiomeric site control (see above).

The model for the stereochemical induction presented above and in Figure 11 can explain the relation between structural variation of the chiral metallocenes **32-35** and their polymerization results given in Table 2, which in turn is a test of the model.

Table 2. Polymerization results of structurally varied bridged metallocenes (data taken from ref. 166)

Metallocene	Activity ^a	$M_w^b \cdot 10^3$	n_{iso}
32 Me ₂ Si(Ind) ₂ ZrCl ₂	115	35	50.1
33 Me ₂ C(Ind) ₂ ZrCl ₂	27	15	11.5
34 Me ₂ Si(3-MeInd) ₂ ZrCl ₂	33	28	2.1
35 Me ₂ Si(C ₅ H ₅)(Ind)ZrCl ₂	6	17	4.6

^a Activity in kg of polypropene per mmol of metallocene - ^b Weight average molecular mass (in g/mol) of polymer determined by GPC - n_{iso} = average isotactic block length by ¹³C NMR spectroscopy

Taking the dimethylsilyl-bridged bis(indenyl) compound **32** as a reference point, then the shortening of the bridge through the introduction of the isopropyl bridge in **33** widens the angle and hence the space between the indenyl ligands. More space means a reduced steric interaction between the ligands and monomer and the chain end. Thus, the energetic difference between the two prochiral positions of the propene monomer (cf. **a** and **b** in Figure 11) is decreased so that more stereoerrors occur and a reduction in stereospecificity is observed. Having methyl substituents on the 3-position of the five-membered ring as in **34** eliminates the energetic difference between **a** and **b** (Figure 11) completely and therefore leads to a total loss of stereospecificity. In the mixed indenyl-cyclopentadienyl metallocene **35**, a larger energetic difference between the prochiral positions only exists upon monomer approach on the side of the six-membered ring. Approach from the other side can then only be controlled through interactions with the chain end.¹⁶⁶

Non-C₂ symmetric or unsymmetrical ansa-metallocene complexes with the cyclopentadienyl-indenyl backbone (**36**) have also been advocated as stereoregular propene polymerization catalysts. Most of these precursors when activated with MAO produce homopolypropenes with excellent thermoplastic elastomeric properties attributable to hemiisotactic microstructures (cf. Figure 8).¹⁶⁷ The term hemiisotactic means that the insertion

of every second (even) propene unit is sterically controlled while the intermediate (odd) insertions occur statistically. Based on the asymmetric $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{Ind})\text{ZrCl}_2$ complex experimental and modelling studies were able to describe such polymer structures.¹⁶⁸ The microstructure of the elastomeric polypropenes produced with these unsymmetrical catalysts is (as expected) sensitive to changes in catalyst structure and temperature but also to changes in pressure.¹⁹⁹ With the appropriate bulky substitution, as shown in **37**, the polymerization of propene was found to afford highly isotactic polymers of medium to high molecular weight with %*mm* > 99.¹⁶⁹ $\text{Ph}_2\text{C}(\text{C}_5\text{H}_5)(\text{Ind})\text{ZrCl}_2$ was a tailored metallocene for the copolymerization of ethene with sterically demanding cycloolefins (see below).¹⁷⁰

Substituted Unbridged Metallocenes: Having bulky alkyl groups attached to the unbridged cyclopentadienyl or indenyl ligands in Cp_2ZrCl_2 led mostly only to atactic and low molecular mass polypropenes (oligomers; see section 9) at conventional polymerization temperatures (above 50 °C) even though the ring rotation is probably hindered.^{154,171} Chiral auxiliaries, such as cholestanyl,¹⁷² neoisopinocampyl,¹⁷³ neomenthyl and neoisomenthyl¹⁷⁴ were attached to unbridged indenyl and tetrahydroindenyl ligands. Only at low temperature the resulting zirconocene complexes (activated by MAO) produce high molecular weight polypropene with enantiomorphic site control. Even from a dimethylsilyl-bridged bis(cyclopentadienyl) complex, where one of the cyclopentadienyl rings carries a neomenthyl group as a chiral auxiliary, the products were of low molecular mass and only at low temperature (0 to -45 °C) was the isotacticity (by *mmmm* pentad) greater than 90%.¹⁷⁵ The neoisomenthyl-substituted systems were found to be much more stereoselective (up to 77% *mmmm* pentad) than the isomeric neomenthyl-substituted systems (maximal 37% *mmmm* pentad). It was assumed that the latter switch back and forth between C_2 - and C_1 -symmetric conformations of the metallocene backbone during catalysis, thereby giving rise to alternating

isotactic and near atactic sequences along the growing polymer chain (cf. to oscillating catalyts below). The role of torsional isomers in these planarly chiral nonbridged bis(indenyl)metal complexes has been investigated by solid state and solution (NMR) structural studies.¹⁷⁴

With the appropriate ligands unbridged group IV metallocene catalysts could, however, polymerize propene to crystalline isotactic polypropene even at conventional polymerization temperatures. Bis(1-methylfluorenyl)zirconium dichloride (**38**) after activation with MAO gave at 60 °C a polymer which was 83% isotactic (*mmmm* pentade). The activity was 1200 g PP/g metallocene in liquid propene. An analysis of the polymer microstructure showed *mrrm/mmrr* sequences which are consistent with an enantiomeric-site stereochemical control mechanism (see above).¹⁷⁶ It is noteworthy here, that a bridged bis(fluorenyl)zirconium complex gave predominantly atactic polypropene, albeit of high molecular mass.¹⁷⁷ When a phenyl group was placed on the C₅ ring (the 9-position) in **38** no propene and only low ethene polymerization activity was observed due to blocking of the insertion path by the bulky 9-substituent.¹⁷⁸

Isotactic-Atactic Block Polymerization, Oscillating Catalyts: The concept is a further development of the use of unbridged bis(indenyl) and -(tetrahydroindenyl) ligands by *Erker et al.* with bulky chiral groups such as cholestanyl,¹⁷² neoisopinocampyl,¹⁷³ neomenthyl and neoisomenthyl¹⁷⁴ attached, so that torsional isomers become possible. New efforts by *Coates and Waymouth* concentrated on phenyl substituted indenyl compounds.¹⁷⁹ Figure 12 shows the essentials of the concept of oscillating catalyts. The phenyl-substituted indenyl rings are free to rotate or oscillate about the metal-ring bond and subsequently lead to the *rac*- and *meso*-rotamer, which consequently exercise a different stereochemical control in propene insertion. The enantiomeric *rac*-rotamer gives the isotactic block sequences, the achiral *meso*-form leads to the atactic polypropene. The block length decreases with increasing temperature and the isotactic block lengthens with increasing pressure.

Syndiospecific Polymerization: C_s -symmetric catalysts of the type **39** where the metal carries a bridged cyclopentadienyl and fluorenyl ligand, yield syndiospecific PP with some isotactic triads (*mm*) as defects. The first report on this remarkable new syndiospecific polymerization with hafnium and zirconium metallocenes appeared in 1988, up to this time syndiotactic PP could only be obtained in vanadium-catalyzed polymerizations below $-50\text{ }^\circ\text{C}$.¹⁸⁰ (For a morphological study on syndiotactic PP prepared by *ansa*-metallocenes, see ref. ¹⁸¹) Figure 13 illustrates the syndiotactic propagation with such a C_s -symmetric cyclopentadienyl-fluorenyl catalyst. Strong evidence for the chain migration with every insertion step (cf. Figure 11) is provided by the syndiotactic polymerization behavior of the C_s -symmetrical catalysts such as **39**. For the syndiotactic polymerization an exchange of chain and monomer positions is a prerequisite because without it meso stereosequences, i.e. an isospecific behavior would be expected.¹⁶⁶ Seemingly small variations in the ligand structure have a significant effect on the stereospecificity¹⁸²: Note that the closely related silylene bridged derivative $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)(\text{Flu})\text{ZrCl}_2$ when activated with MAO catalyzed non-stereospecific propene polymerization without any syndiotactic tendency.^{183,184} An additional methyl substituent on the cyclopentadienyl ring in **39** (in β -position relative to the bridge) gives a complex that polymerizes propene in a di-stereospecific manner to give syndiotactic-isotactic stereoblock PP,¹⁸⁵ a *tert*-butyl ligand gives an isotactic-specific metallocene complex.¹⁸⁶ Substituents on the sterically little active positions 2 and 7 of the fluorenyl moiety (cf. numbering in **39**) do not affect the syndiospecificity of the catalyst but have large effects on the activity.¹⁸⁷ With no bridge present in **39**, or ligand substituted derivatives thereof, only atactic propene is formed, believed to arise because the C_s symmetry of the catalyst, necessary for syndiotactic polymerization, is not present anymore owing to the unhindered rotation or oscillation of the fluorenyl ligand.¹⁸⁸ The influence of substituents on the bridge-head atom in

$RR'(C_5H_5)(Flu)ZrCl_2/MAO$ on the propene polymerization activity has been studied and found to increase in the order $MeMe \approx MePh \approx (CH_2)_4 < HH < HPh < (CH_2)_5 < PhPh$. The PP molecular mass is much higher (by a factor of five or six) for $RR' = MePh$ or $PhPh$.¹⁸⁹

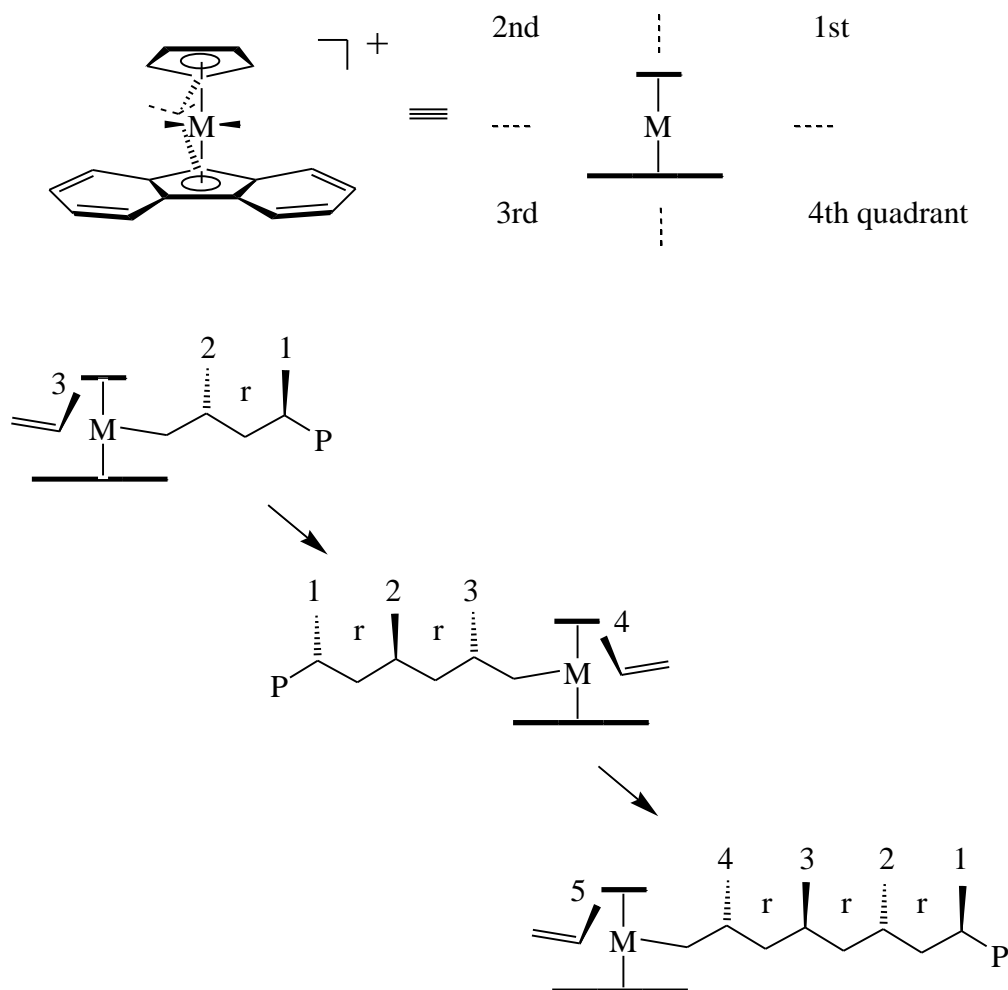


Figure 12

Enantiomer Separation and Enantioselective Polymerization: Since the propene polymerization is usually carried out only in a stereoselective and not an enantioselective manner, it suffices to use the racemic mixture of the pre-catalyst. The enantiomers differ only in that they form polypropene chains of different (left or right) helical handedness.¹⁹⁰ Enantiomer

separation of the pre-catalyst was shown to be possible by *Brintzinger et al.* using the enantioselective reaction of the (*S,S*)-form of racemic $C_2H_4(IndH_4)_2TiCl_2$ (cf. **7**) with 0.5 equivalents of (*S*)-(-)-1,1'-bi-2-naphthol in the presence of an excess of sodium metal to give the (*S,S*)-binaphtholate derivative (cf. **50** in section 12). After separation by chromatography the pure diastereomer is cleaved by treatment with gaseous HCl to return to $C_2H_4(IndH_4)_2TiCl_2$ yet solely in its (*S,S*)-form.⁴⁴ Similarly the racemic mixture of the zirconium derivative was resolved and the pure (*S,S*) zirconocene enantiomer was employed in propene polymerization. In the resulting polymer the atactic parts were decreased and the isotactic sequence length raised further compared to the racemic catalyst mixture. Furthermore optically active polypropene could be obtained for the first time under certain conditions (no dissolution or melting of the sample).^{40,191} Using this enantiomer for the oligomerization of 1-butene yielded the optically active dimer 3-methylheptane and the trimer 3-methyl-5-ethylnonane in an optical purity of 70-80%.¹⁹² The (*S,S*)-form of $C_2H_4(IndH_4)_2ZrCl_2/MAO$ was also used in the copolymerization of cyclopentene with allyltrimethylsilane; the copolymer obtained shows a small optical rotation which may result from the cyclopentene units only.¹⁹³

Comparative Polymerizations involving propene with a larger series of metallocene derivatives are again rare. An illustrative example to the contrary was provided by *Kaminsky, Spaleck et al.* who compared the catalytic activity of two unbridged and nine ansa-metallocenes together with the resulting polymer properties using a constant set of polymerization parameters.¹⁵² Selected data of this study is provided in Table 3.

Table 3. Activities of a series of eleven catalysts in polymerization of propene, statistical isotacticities *I*, fraction of heterotactic triads *H*, and viscosity-averaged molecular weight M_η (data taken from ref. 152)

Catalyst	Activity ^a	$M_n \cdot 10^3$	I^b	H^c
A, <i>rac</i> -Me ₂ Si(Ind) ₂ ZrCl ₂	1 940	79	0.97	0.04
B, <i>rac</i> -Ph ₂ Si(Ind) ₂ ZrCl ₂	2 160	90	0.97	0.05
C, <i>rac</i> -(PhCH ₂) ₂ Si(Ind) ₂ ZrCl ₂	270	72	0.95	0.02
D, <i>rac</i> -Me ₂ C(C ₅ H ₄ Me)(Ind)ZrCl ₂	400	4	0.54	0.49
E, <i>rac</i> -Me ₂ C(C ₅ H ₅)(Ind)ZrCl ₂	180	3	0.49	0.54
F, <i>rac</i> -C ₂ H ₄ (Ind) ₂ ZrCl ₂	1 690	32	0.95	0.09
G, <i>rac</i> -C ₂ H ₄ (Ind) ₂ HfCl ₂	610	450	0.94	0.08
H, <i>rac</i> -C ₂ H ₄ (IndH ₄) ₂ ZrCl ₂	1 220	24	0.98	0.02
I, Me ₂ C(C ₅ H ₅)(Flu)ZrCl ₂	1 550	159	0.94 ^d	0.10
J, (C ₅ H ₅) ₂ ZrCl ₂	140	2	0.56	0.75
K, (C ₅ H ₄ Nm) ₂ ZrCl ₂ ^e	170	3	0.69	0.52

^a Activity in kg of polypropene per mol of metallocene and per h, standardized to equal monomer concentration - ^b isotacticity $I = (mm) + 0.5 (mr)$ - ^c heterotacticity $H = (mr) -$ ^d syndiotacticity $S = (rr) + 0.5 (mr)$; with (mm) , (rr) and (mr) representing isotactic, syndiotactic and heterotactic triad fractions - ^e Nm = neomenthyl

The data in Table 3 indicates that the chiral bis(indenyl) systems are highly isospecific and the C_s-symmetric fluorenyl-cyclopentadienyl system (I) is highly syndiospecific (see above). The compounds D and E are chiral but lack C₂-symmetry (see above), hence are of a reduced stereospecificity. The unbridged species K with its bulky substituents produces stereoblock PP similar to the system **31** described earlier. The complexes D, E, J, and K, which lack a high degree of stereospecificity, show poor activity and give only low molar mass or oligomeric materials (see section 9). From this it is deduced that with the prochiral monomer propene, the stereospecific polymerization mode is strongly favored over the aspecific one, thereby clearly overcompensating steric influences coming from metallocene structure (cf. also the "advanced metallocenes", discussed below). Hafnocenes are known to be less active than their zirconocene analogues but produce much higher molar mass polymers (G versus F). Similarly, syndiospecific catalysts (I) lead to higher M -values compared with isospecific analogues.¹⁵²

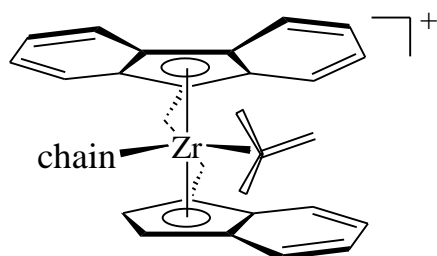
It is important to note that C₂-symmetry is necessary but not sufficient for high isospecificity and that activity and stereospecificity are directed by the same factors in propene

polymerization with stereorigid metallocenes.¹⁹⁴ The data in Table 2 and 3 illustrate that a reduction of stereospecificity is accompanied by a reduction of catalyst activity towards propene and lowering of the polymer molecular mass.¹⁶⁶

Stereoregularity - Pressure Dependence and Chain-End Epimerization: For propene polymerization besides the obvious variables such as temperature, type of catalyst, Al/Zr concentration and the like, it was demonstrated that a decreasing monomer concentration (below 2 mol/l) at a given temperature lead to a lower stereospecificity of the polypropene formed by C_s - and C_2 -symmetric *ansa*-metallocene catalysts,^{195,196} eventually yielding atactic propene oligomers when the monomer concentration approaches zero. It is suggested that this effect of monomer concentration on propene polymerization parameters is the primary cause for many of the conflicting literature data on propene polymerization.¹⁹⁷ As a possible explanation a slow reaction of epimerization was suggested to compete with the monomer insertion. The change of configuration (or epimerization) at the last inserted unit might proceed through a β -hydrogen elimination with the olefin remaining coordinated, olefin rotation and reinsertion into the Zr-H bond to give a secondary alkyl complex, followed by another hydrogen elimination (from one of the methyl groups) and olefin reinsertion to return to the now primary alkyl chain but now with a racemized end group.¹⁹⁶ Thus, besides propene insertions with the wrong enantioface, the isomerization of the growing chain end can give rise to stereoerrors. This was recently supported by polymerization experiments with isotope labeled propene-1-*d*¹²² and propene-2-*d*¹⁹⁸ which found that most stereoirregular monomeric units in the isotactic polypropene obtained by C_2 -symmetric catalysts are deuterated at the methyl group.

With unsymmetric *ansa*-catalysts (**36** and **40**) it was, however, observed that an increase in monomer concentration (pressure) mostly led to a decrease in stereoregularity of the polypropene produced.^{199,200} This dependence is discussed on the basis of differently chain-

ligated species for the catalyst type **40**; if the chain preferentially occupies the open space (as indicated) then insertion of the propene monomer through the aspecific site between the two six-membered rings will be more important at high pressure and lead to more stereoerrors in the chain.²⁰⁰ (Consequently, it should be noted that in another study the type **36** unsymmetric catalyst did not show a dependence in stereoregularity upon pressure.²⁰⁰)

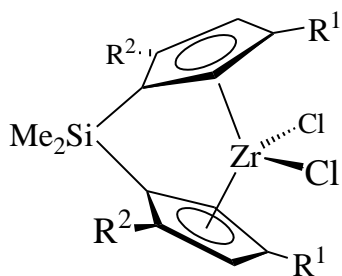
**40**

Bridge Modifications: Studies also involved changes in the bridge, e. g. substituting the hydrogen atoms in the ethanediyl or the methyl groups in the dimethylsilyl bridge. One approach involved the introduction of additional stereocenters in the bridge, either by an unsymmetrical ethanediyl substitution pattern²⁰⁰ or by converting Me_2Si to a di(menthoxy)silylene, a silolene or a (1,3-propanediyl)silylene bridge.²⁰¹ The idea behind substituting the bridge moiety is to influence the ethanediyl bridge conformation, allow for the isolation of a single diastereomer and to effect polymerization parameters. The effect on the stereoselectivity is, however, much less pronounced compared to substitutions directly on the cyclopentadienyl or indenyl moiety. Bigger effects for the bridge-modified derivatives were observed on molecular mass, tolerance of catalyst and the deactivation process.²⁰¹ The bridge atom was also varied from silicon to germanium^{202,184} to tin²⁰³ and the polymerization behavior of the resulting complexes investigated. A decrease in tacticity is observed going from Si to Ge.¹⁸⁴ The activity for the Si and Sn bridged species in ethene polymerization was found comparable, yet with Sn the rate of chain transfer decreased significantly.²⁰³

Molecular Mass Enhancement, Advanced Metallocenes: For a long time it was a serious drawback that even chiral zirconocene/MAO catalysts produced only low molar mass oligomers at conventional polymerization temperatures above 60 °C, where the activity was high (see also section 9, olefin oligomerization).^{40,159,204} The reason for obtaining oligomeric or low molar mass polymeric products is due to a larger increase of the rate of chain transfer (k_T , mainly by β -hydrogen elimination) versus the rate of chain propagation (k_P) with the increase in temperature. The mean degree of polymerization, P_n , which is proportional to the number average molecular mass M_n is given by the ratio of the growth rate to the rate of transfer, $M_n \sim P_n \approx k_P/k_T$.

First, this disadvantage was tried to counter by using chiral hafnium metallocene catalysts, such as *rac*-C₂H₄(Ind)₂HfCl₂ and *rac*-C₂H₄(IndH₄)₂HfCl₂, activated with MAO. These hafnium catalysts provided high molar mass polypropene which was also slightly more stereoregular than those obtained with zirconium.²⁰⁵ However, their yields remained too low in comparison to zirconium catalysts.

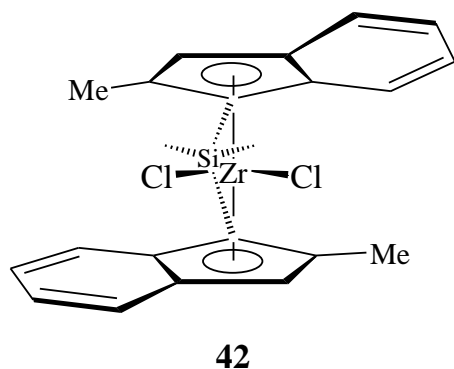
A clue for directed modifications to block the path and decrease the rate of chain transfer was seen in comparative propene polymerizations involving chiral, 2,4-alkyl-substituted cyclopentadienyl ansa-zirconocenes (**41**). With R¹ = *t*Bu longer chains were obtained than with R¹ = *i*Pr. This was traced to the increased steric repulsion between the more bulky *t*Bu group and the chain end upon formation of the β -H-Zr bridge necessary for chain transfer.²⁰⁸



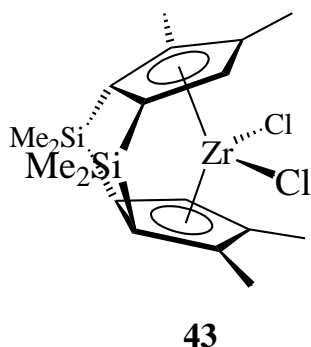
$R^1 = iBu, iPr; R^2 = H, Me$

41

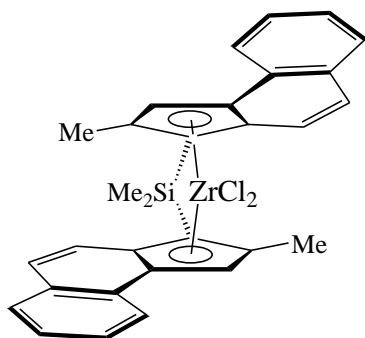
It was soon recognized that the additional presence of methyl substituents on the five-membered ring in ansa-bis(indenyl) ligands and their position was highly influential in optimizing not only the tacticity but also the polymer molar mass at elevated temperature. The C_2 -symmetric metallocenes bearing methyl groups at the 2-(α -)position (adjacent to the bridge) (**42**) gave polymers in higher yield and of the higher stereospecificity.²⁰⁶ The same was already found earlier for ansa-bis(cyclopentadienyl) systems.^{207,208} The remarkable effect of the α -methyl substituents may be traced to the suppression of 2-1- or tail-to-tail (mis)insertions (cf. Scheme 7). Without the α -methyl group such misinsertion can be found with a magnitude of 1.5%, whereas in the α -methyl substituted complexes (just as in the classical heterogeneous Ziegler-Natta catalysts) these regio-irregularities are suppressed close to or below the detection limit.²⁰⁸ On the other hand, the methyl group is turned away from catalytically relevant space, so that a direct steric effect on chain transfer and subsequently molecular mass of the polymer may not necessarily follow. Instead, an electron donating effect was proposed, which decreases the Lewis-acidity on the cationic center, thereby reducing the tendency for β -hydrogen abstraction, so that the number of chain-transfer reaction is reduced and the molar mass increases.²⁰⁶



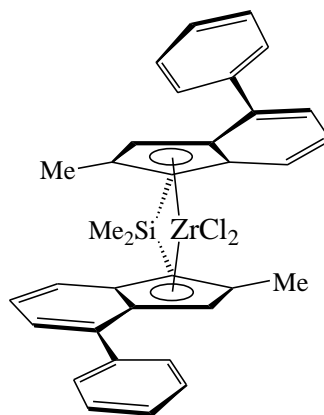
In addition, the increase in stereoselectivity brought about by the α -methyl substituents in chiral metallocene catalysts is connected to a decreased tendency of these α -substituted complexes to undergo thermally induced excursions from C_2 -axial symmetry.²⁰⁹ To a degree which depends on their substitution pattern *ansa*-metallocene complexes are fairly easily deformable. The bridged ligand framework can rotate up to $\pm 20^\circ$ about the metal- C_5 -ring-centroid axes between two shallow energy minima leading to off- (C_2) -axially distorted conformers. Figure 14 sketches these two conformations for which an energy difference of 0.95 kcal/mol was deduced from temperature-variable NMR, with the Y (indenyl-backward) conformation suggested to be the "higher" energy conformer.²¹⁰ An unrestricted fluctuation in solution between these two conformations has implications for structure-function correlations in olefin polymerization.²⁰⁹ These studies apparently have led to the synthesis of doubly bridged zirconocenes, e.g. **43**. According to one study, intact **43** does not appear to possess catalytic activity but in combination with MAO is slowly degraded to give a catalytically active species for propene polymerization,²¹¹ while another study describes the ethene and propene polymerization activity (atactic oligomers with propene) and does not mention a degradation.²¹² A theoretical study finds doubly-bridged *ansa*-zirconocenes based on the norbornadiene skeleton with suitable substitution highly stereospecific.²¹³ Doubly bridged titanocene and zirconocene complexes containing two ethanediyl ($-C_2H_4-$) bridges have also been described,²¹⁴ but we are not aware of a report on their polymerization activity.



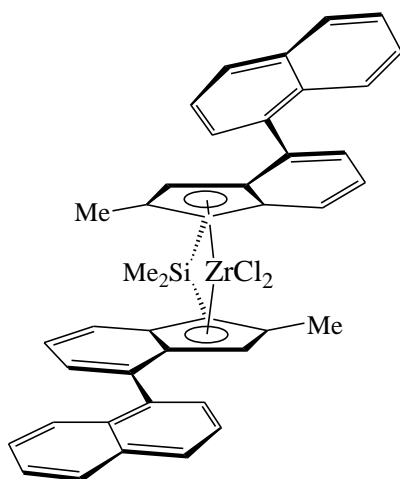
Eventually the problem of oligomeric molecular mass of polypropene at conventional reaction temperatures of 50 °C and higher seemed to have been finally overcome with the introduction of *ansa*-zirconocene complexes carrying additional aromatic substituents on the six-membered indenyl moiety, either annelated as in $\text{Me}_2\text{Si}(2\text{-Me-benz}[e]\text{indenyl})_2\text{ZrCl}_2$ (**44**)¹⁴⁵ or sigma-bonded in appropriate positions as in $\text{Me}_2\text{Si}(2\text{-Me-4-phenylindenyl})_2\text{ZrCl}_2$ (**45**) or in $\text{Me}_2\text{Si}\{2\text{-Me-4-(1-naphthyl)indenyl}\}_2\text{ZrCl}_2$ (**46**).¹⁴⁶ The complexes **44-46** are examples of the so-called "advanced metallocenes" which give activities, stereospecificities and polypropene molecular masses much higher than those of any previously described metallocene system.¹⁴⁶ The annelated benz[e]indenyl in **44** compared to the standard *ansa*-bis(indenyl) system leads to a considerable gain in activity because the **44**/MAO catalyst is deactivated at an unusually low rate with an about 3 times longer half-life. Here again, a direct comparison of the complex **44** with and without α -methyl substituents revealed the molecular mass enhancing properties (by a factor of 4) of the methyl groups, although some of the activity was lost again.^{145,215}



44



45



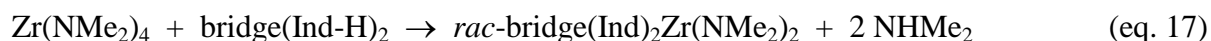
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The polypropene molar mass from polymerization with e.g. $C_2H_4(Ind)_2ZrCl_2/MAO$ can be lowered by the addition of hydrogen through the hydrogenolysis reaction. The catalyst activity was also found to improve in the presence of hydrogen, the molecular mass distribution remained unchanged.²¹⁶

Molecular Modelling: A variety of theoretical modeling studies are available (in addition to those already mentioned in the text) which in a valuable interplay between experiment and theory substantiated or adjusted the initial hypotheses on the stereocontrol in the α -olefin polymerization with the various stereospecific catalysts¹⁶⁸, e.g. ab initio MO and molecular

mechanics (MM) studies on specificity control in propene polymerization with bridged metallocenes;²¹⁷ an MM study on the back-skip of the growing chain at model complexes for various ethanediyl-bridged metallocenes;²¹⁸ a DFT-study on the influence of rotation between agostic structure on ethene interaction with a zirconocene polymerization site;²¹⁹ a force-field study on π -stacking as a control element in the oscillating (2-PhInd)₂ZrCl₂ catalysts;²²⁰

In view of the eminent importance of *ansa*-metallocenes for α -olefin polymerization, an efficient synthetic route is worthwhile noting: In an amine elimination reaction Zr(NMe₂)₄ reacts with bridged bis(indenes) to yield the corresponding *ansa*-bis(indenyl)zirconium dimethylamido complexes (equation 17). The reaction not only proceeds in high yield but also gives in high excess the racemic mixture versus the achiral meso form.²²¹



bridge = Me₂E (E = C, Si); CH₂CH₂

8. Homopolymerization of Other α -Olefins

In catalytic alkene polymerization with metallocene catalysts the molar masses of the obtained polyalkenes and the reaction rates decrease in the order ethene > propene > 1-butene > 1-pentene > 1 hexene.

1-Butene: The system *rac*-C₂H₄(IndH₄)₂ZrCl₂/MAO polymerizes the monomer with high activity [2640 kg polybutene/(mol Zr · h) at 20 °C] to an isotactic and waxy-crystalline material of $M_n = 50 - 150\,000$.¹⁵⁹ From *rac*-Me₂Si(IndH₄)₂ZrCl₂/MAO a lower molecular mass oligomer ($M_n \approx 2000$) was obtained whose end group structure was analyzed in terms the reaction mechanism of initiation and propagation with various chain-transfer reactions.²²² A ¹³C NMR study on the regiospecificity of isotactic 1-butene polymerization by C₂-symmetric metallocenes provided evidence on the occurrence of 1,4 1-butene enchainments.^{134,223}

1-Pentene: Crystalline, syndiotactic poly(1-pentene) was obtained with good polymerization activity ($5 \cdot 10^3$ kg of polymer per mole of zirconium per hour) using the syndiospecific catalyst $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{Flu})\text{ZrCl}_2/\text{MAO}$.²²⁴

1-Hexene: MAO-activated *rac*- $\text{C}_2\text{H}_4(\text{Ind})_2\text{ZrCl}_2$ yields highly isotactic polyhexene and also in various solvent but with M_n only around 20 000 even at low temperatures.²²⁵ Poly(1-hexene) with high molar mass (above 10^6 g/mol for M_w) could be obtained through the application of pressures over 100 and up to 1000 MPa with achiral Cp-methylated zirconocene and hafnocene/MAO catalysts.²²⁶

3-Methyl-1-butene: C_2 -symmetric metallocene/MAO catalysts give isotactic poly(3-methyl-1-butene) with reasonable productivities, contrary to earlier literature reports. A prevailing isotactic polymer was also obtained by C_s -symmetric metallocenes, which normally are syndiospecific in propene polymerization.²²⁷

9. Olefin Oligomerization

The oligomerization of α -olefins has also been investigated. Initially the finding of low-molar-mass products from propene polymerization with zirconocene catalysts was generally regarded as unfortunate.^{40,43,159,163,228,229} Now, it is more and more recognized that metallocene catalysts may be used effectively for the directed oligomerization of α -olefins^{154,230,231,232,233,234} to give oligomers with almost exclusively double-bond end groups, predominantly of the vinylidene type. The use of olefin oligomers as intermediates for specialty chemicals drives the interest in the catalytic oligomerization.²³⁵ A variety of functionalization reactions with this double bond are possible leading to organic specialities with possible applications as adhesives, blend compatilizers,²³⁶ fragrances, lubricants, additives for fuels or in the paper and leather industry.²³⁰ Also, α -olefin oligomers or derivatives thereof can be used as (macro)monomeric building blocks for novel graft copolymers containing oligo-olefin side chains.²³²

Olefin oligomerization is also used to study mechanistic aspects of metallocene catalysis because of the homogeneity of the system (no heterogenation through polymer precipitation) and because the oligomeric products are easier to analyze than high-molar-mass polymers.^{162,237,238,239} At the limit of oligomerization one encounters the use of metallocene Ziegler systems as carbon-carbon coupling catalysts in organic synthesis, e.g. for the dimerization of olefins.^{154,234,240}

10. Copolymerization

Comonomer insertion into the polymer chain is solely statistical for polymers obtained with metallocene catalysts (proven by NMR), contrary to conventional Ziegler-Natta catalysis where the comonomer is mainly incorporated into the low molar mass fraction.

With $(C_5H_5)_2ZrCl_2/MAO$ the copolymerization of ethene and propene²⁴¹ or 1-butene gives elastomers with different properties. Copolymerization of ethene with 1,3-butadiene yields polyethenes which are functionalized by olefinic groups;⁴¹ along the same lines copolymerization of ethene with 5-vinyl-2-norbornene using $(C_5H_5)_2ZrCl_2/MAO$ occurs with regioselective insertion of the endocyclic double bond into the polymer chain, leaving the exocyclic vinyl double bond as a pendant unsaturation which can be readily converted to the hydroxy/epoxy group.²⁴² Copolymerizing ethene with 4-vinylcyclohexene with $Ph_2C(C_5H_5)(Flu)ZrCl_2/MAO$ allowed hydroboration of the pendant cyclohexene double bond and oxidative workup yielded polyalcohols.²⁴³ 4-Methyl-1-pentene was copolymerized with ethene using a chiral and an achiral catalyst.¹⁹¹ Also, in ethene/propene or 1-hexene copolymerization, the stereospecific $rac-C_2H_4(Ind)_2ZrCl_2$ and $rac-C_2H_4(IndH_4)_2ZrCl_2$ exhibit much higher polymerization activities than simple unbridged metallocene catalysts as revealed in a comparative study. The former gave copolymers having comonomer compositions similar to the feed composition whereas nonbridged catalysts favored the incorporation of ethene over

propene (1-hexene).²⁴⁴ In another comparative study the activities in ethene/1-hexene and 1-octene copolymerization were found to be similar.²⁴⁵ At a 1:1 ethene/propene feed ratio $(C_5H_5)_2ZrCl_2/MAO$ gave rather low molecular mass copolymers ($M_n < 10\,000$ g/mol) above 40 °C; the molar mass increased with decreasing temperature and with higher ethene feed.²⁴⁶

Small amounts of ethene comonomer content in propene (homo)polymerization lead to polymers with two times higher molecular weights and only slightly lower melting points. The increase in chain length is due to an activation of the catalytic sites by ethene insertion which were blocked by a preceding 2-1 insertion which normally leads to β -hydride elimination and chain growth termination.¹³³ The ethene/1-hexene copolymerization of homogeneous zirconocene and a classical supported $TiCl_3$ catalyst were compared to investigate the influence of α -olefin on the enhancement of ethene polymerization rate (the "comonomer effect"). The metallocene/MAO systems were both found to show a reduction in ethene activity upon comonomer addition, contrary to the classical $TiCl_3$ catalysts²⁴⁷ as well as a rate enhancement.²⁴⁸ The copolymer properties of ethene/2-allylnorbornane prepared by $TiCl_4/Al\ iBu_3$ and $(C_5H_5)_2ZrCl_2/MAO$ were compared and the metallocene copolymer found homogeneous and random in nature while the classical Ziegler-Natta catalyst gave a heterogeneous and blocky copolymer.²⁴⁹

Ethene was copolymerized with 1-dodecene and 1-octadecene to study the influence of the comonomer chain length on the rate enhancement effect with the catalysts $Me_2C(C_5H_5)(Flu)ZrCl_2$ or $Me_2Si(Ind)_2ZrCl_2/MAO$.²⁵⁰ A comparative ethene/1-octadecene copolymerization study between $(C_5H_5)_2ZrCl_2$ and $(C_5H_5)_2HfCl_2/MAO$ showed the hafnocene to be more reactive towards 1-octadecene and giving higher molecular masses of the polymer but at a lower total activity.²⁵¹ With $(C_5H_5)_2ZrCl_2/MAO$ ethene has been copolymerized with 1-octene, 1-tetradecene and 1-octadecene for a comparison of the copolymer properties.²⁵² $Me_2C(C_5H_5)(Flu)ZrCl_2$ has been used to investigate the influence of temperature in the

ethene/1-hexene or 1-octadecene copolymerization.²⁵³ Ethene-styrene copolymers have been prepared with a catalytic system based on $\text{Me}(\text{Ph})\text{C}(\text{C}_5\text{H}_5)(\text{Flu})\text{ZrCl}_2/\text{MAO}/\text{TMA}$.²⁵⁴

A propene/1-octene copolymerization with the syndiospecific catalyst $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{Flu})\text{ZrCl}_2/\text{MAO}$ showed again random incorporation of large amounts of 1-octene. The polymer parameters were studied as a function of octene content.²⁵⁵ In a series of copolymerizations of propene with higher α -olefins including 1-butene, 1-hexene, 1-octene, 1-dodecene, and 1-hexadecene with the isospecific catalyst $\text{C}_2\text{H}_4(\text{Ind})_2\text{HfCl}_2/\text{MAO}$, the products obtained are random copolymers and the reactivity of the higher α -olefins in the copolymerization decreases only slightly with increasing length of the olefin.²⁵⁶

11. Polymerization and Copolymerization of Cyclic Olefins

The metallocene/MAO catalyst systems allow polymerization of cyclic olefins with no ring opening taking place.²⁵⁷ With chiral metallocenes, cycloolefines like cyclobutene, cyclopentene, and norbornene can be polymerized to give isotactic polymers. The opening of the double bond can take place in a cis or a trans fashion, so that four microstructures can be distinguished cis-iso/syndiotactic and trans-iso/syndiotactic (cf. Figure 15 or **51**). For polycyclopentene, contrary to the initial formulation as a 1-2 insertion product **47**¹⁹³, it was later proven that incorporation proceeded in cis- and trans-1-3 manner (Figure 15) to give poly(1,3-cyclopentane).²⁵⁸ From $\text{C}_2\text{H}_4(\text{Ind})_2\text{ZrCl}_2$ and cyclopentene isotactic polycyclopentene is obtained which is insoluble in aromatic or aliphatic hydrocarbons and highly crystalline with a melting point above the decomposition temperature.¹⁹²

The polycycloalkenes show extremely high melting points which lie above their decomposition temperatures (in air). Under vacuum the melting points were found (by DSC) to be 485 °C for polycyclobutene, 395 °C for polycyclopentene, and over 600 °C for polynorbornene.¹⁹³ Such high melting points make the homopolymers difficult to process. To

lower the melting points, the cycloolefin can be copolymerized with ethene or propene, thereby it was possible with metallocene catalysts to solve a decade old problem, namely the technical synthesis of cycloolefin-copolymers.^{2,257} As pointed out above for the copolymers there is a random distribution of the cycloolefine units in the polymer chain according to ¹³C-NMR measurements. In comparative cycloolefin/ethene copolymerization experiments the activity and the incorporation of the cyclic olefin is much higher with the chiral catalyst than with the achiral (C₅H₅)₂ZrCl₂.¹⁹³ Copolymerization of cyclopentene with allyltrimethylsilane using the (*S,S*) enantiomeric form of C₂H₄(IndH₄)ZrCl₂ gave an optically active copolymer.¹⁹³

The rigid tetracyclododecene ("dimethanooctahydronaphthalene") (**48**) was copolymerized with ethene using chiral and achiral catalysts and the amorphous product with up to 12%, later up to 33%²⁵⁹ of the cycloolefin featured a high glass-transition temperature, excellent transparency, thermal stability and chemical resistance.¹⁹³ The same holds for the norbornene/ethene copolymer and it is suggested that these materials could be used for optical discs and fibers. With C₂H₄(IndH₄)ZrCl₂/MAO ethene is inserted only 1.5 to 3.2 times faster than norbornene and copolymers containing more than 50 mol% of norbornene units can be made; if the norbornene concentration is higher than 60 mol% as glass transition point of about 120 °C can be reached.²⁶⁰ On the basis of a norbornene/ethene copolymer, the companies Hoechst and Mitsui Sekka have developed a highly transparent technical plastic, called TOPAS (*thermoplastic olefin polymer of amorphous structure*). The properties of TOPAS open applications in the market of compact disks and magneto-optic storage disks.² In a comparative study with R₂C(C₅H₅)(Flu)ZrCl₂ compounds, the asymmetric complex Ph₂C(C₅H₅)(Ind) proved to be the tailored metallocene for the copolymerization of ethene with sterically demanding cyclic olefins, such as **48** and **49**.¹⁷⁰

Copolymerization of ethene with 5-vinyl-2-norbornene using (C₅H₅)₂ZrCl₂/MAO occurs with regioselective insertion of the endocyclic double bond into the polymer chain, leaving the

exocyclic vinyl double bond as an unsaturation which can be readily converted to the hydroxy/epoxy group.²⁴²

12. Diene- and Cyclopolymerization

Copolymerization of ethene with 1,3-butadiene or 5-vinyl-2-norbornene yields polyethenes with pendant olefinic groups, which can be further converted to give functional olefins.^{41,242} *rac*-C₂H₄(Ind)₂ZrCl₂/MAO is an excellent catalyst for the ethene (E), propene (P) and ethylidene norbornene²⁶¹ or octa-1,6-dienes (from biomass)²⁶² (D, as diene) terpolymerization with as much as 20 % D uniformly incorporated into the EPDM-terpolymer. EPDM terpolymers with the same components could also be prepared by means of (C₅H₅)₂ZrMe₂/MAO.²⁶³

Cyclopolymerization of 1,5-hexadiene (equation 18) with either of the enantiomeric forms of C₂H₄(IndH₄)ZrBINOL (BINOL = 1,1'-bi-2-naphtholate) (**50**) yields either one of the enantiomeric forms of optically active poly(methylene-1,3-cyclopentane). For poly(methylene-1,3-cyclopentane) four microstructures are possible, which are sketched in **51**. Of these, only the trans-isotactic structure contains no mirror plane (perpendicular to the chain) and is thus already chiral because of its main-chain stereochemistry. A reversibly decreasing molar optical rotation with increasing temperature indicates, however, that the polymer adopts chiral (helical) conformations which may contribute all or in part to the observed optical activity.²⁶⁴

A novel polyspirane (**52**) has been obtained by ring-opening - "zipping up" (= cyclo-) polymerization of methylenecyclopropane with [(C₅Me₅)₂ZrMe]⁺[MeB(C₆F₅)₃]⁻. It is assumed that at some point the initial ring-opening polymerization (equation 19) is replaced through the competing intramolecular C=C bond insertion (equation 20) with the spirocyclization process continuing along the chain.²⁶⁵ When organolanthanide catalysts {(C₅Me₅)₂LnH}₂ (Ln = Sm, Lu)

were employed only the ring-opening to exo-methylene functionalized polyethenes was observed.¹¹¹

A further example of cyclopolymerization can be found in section 13 with 4-trimethylsiloxy-1,6-heptadiene (**56**) (equation 21).²⁶⁶

13. Polymerization of Polar Monomers

The use of group IV metallocenes as initiating systems for the synthesis of polar or functional monomers has also been reported. Although, here in most cases it is more reasonable to assume not a Ziegler-Natta type insertion but a cationic polymerization reaction. For methyl methacrylate (MMA) which can be efficiently polymerized stereospecifically using a two-component catalyst system comprised of $(C_5H_5)_2ZrMe_2$ and $[(C_5H_5)_2ZrMe(THF)][BPh_4]$ the mechanism probably involved enolate complexes in a group-transfer polymerization.²⁶⁷ On the other hand $(C_5H_5)_2ZrMe_2$, *rac*- $C_2H_4(Ind)_2ZrCl_2/Ph_3CB(C_6F_5)_4$, *rac*- $C_2H_4(IndH_4)_2ZrCl_2/Ph_3CB(C_6F_5)_4$ and *rac*- $Me_2Si(Ind)_2ZrCl_2/Ph_3CB(C_6F_5)_4$ were found to be inactive towards the polymerization of MMA without the addition of a Lewis acid such as dialkylzinc and alkylaluminum compounds.²⁶⁸ $Me_2C(C_5H_5)(Flu)ZrCl_2$ failed to initiate the polymerization of MMA even under these conditions.^{268c} The polymerization of polar monomers such as alkyl acrylates can also be initiated by group III and lanthanoide metallocenes e.g. $(C_5Me_5)_2LnMe(THF)$ ($Ln = Y, Sm, Yb$), $\{(C_5Me_5)_2SmH\}_2$ and $(C_5H_4Me)_2Ln(DME)$ to give high molecular weight polymers with extremely narrow molecular mass distribution.¹¹²

Typical C_2 -symmetrical *ansa*-zirconocene catalysts, such as *rac*- $Et(Ind)_2ZrMe_2 / [Ph_3C][B(C_6F_5)_4]$ together with (bis(2,6-di-*tert*-butyl-4-methylphenoxy)methyl)aluminum as the activator were reported for the synthesis of predominantly isotactic poly(*tert*-butylacrylate) (**53**) and highly isotactic poly(methyl methacrylate).²⁶⁹ Cationic group IV metallocene catalysts

derived from the reaction of $(C_5Me_5)_2ZrMe_2$ or $C_2H_4(IndH_4)_2ZrMe_2$ with $B(C_6F_5)_3$ or $[N,N$ -dimethylanilinium] $[B(C_6F_5)_4]$ are active catalysts for the homopolymerization of α -olefins containing silyl-protected alcohols (**54**) and tertiary amines (**55**). With 4-trimethylsiloxy-1,6-heptadiene (**56**) cyclopolymerisation occurs (equation 21).²⁶⁶

Copolymers of propene and the polar monomer **57** were obtained with *rac*- $Me_2Si(IndH_4)_2ZrCl_2/MAO$, containing from 1.3 to 5.5 wt.% of comonomer. The addition of the sterically hindered phenolic monomer (or 2,6-di-*tert*-butylphenol) even increased the catalytic activity, which was attributed to the ability of the shielded phenol unit to function as a weakly coordinating anion.²⁷⁰ Ethene could also be copolymerized with 10-undecen-1-ol using $(C_5H_4$ -*n*Bu) $_2ZrCl_2/MAO$; the bimodal molar mass distribution curve of the polymers obtained indicated, however, the presence of two or more active sites in the catalyst.²⁷¹

14. Recent Trends in Ligand and Metallocene Catalyst Design

This section summarizes novel types of cyclopentadienyl ligands or ligands closely related to the Cp group which were recently used in the synthesis of group-IV metallocenes and their catalytic application in olefin polymerization. Cyclopentadienyl systems with an additional donor function in a side chain, e.g. dialkylaminoethylcyclopentadienyl (**58**) are attracting increased interest.²⁷² It is suggested *inter alia* that the donor atom may reversibly coordinate to and block a vacant coordination site at the metal center, thereby modulating the activity and catalyst lifetime. In a similar direction go studies on disiloxane bridged cyclopentadienyl- or indenyl-metallocene catalysts (**59**) for olefin polymerization. These latter complexes polymerize ethene only with MAO as a cocatalyst, propene with either MAO or $[Ph_3C][B(C_6F_5)_3]$. Towards propene the activity is moderate and increases strongly with temperature when MAO is used as an activator. Even when C_2 -symmetric catalysts such as **59** are employed only atactic

polypropene is obtained. These catalytic effects were interpreted in terms of σ donation from the oxygen atom of the siloxane bridge to the metal center.²⁷³

The 2-siloxy- or 2-dimethylamino-substituted indenyl ligand (**60**) in bridged and unbridged zirconocene complexes and their application in polymerization catalysis has been investigated for its changed electronic properties.²⁷⁴ The zirconium compounds **61** and **62**, where the cyclopentadienyl rings have been formally substituted by the isoelectronic (amino)boratabenzene ligand, can also be activated with MAO for olefin polymerization.²⁷⁵ The use of borate-substituted dianionic cyclopentadienyl ligands gives anionic group IV metallocene complexes (**63**) from which zwitterionic ethene polymerization catalysts are obtained upon activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.²⁷⁶

The homo- and heterodinuclear *ansa*-zirconocene and hafnocene complexes (**64**) were synthesized and their activity as catalysts (activated by MAO, $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$) for the polymerization of ethene and propene has been evaluated. As far as polyethene activity is concerned no advantage rather a negative effect of the incorporation of a second metal is seen. In the case of propene, atactic oligomers are obtained and the activity is higher for the di-zirconocene than for the mononuclear compound.²⁷⁷ We would suggest that the activity trends are due to an increased steric hindrance for ethene but higher stereospecific environment for propene (see above). Another study on a possible cooperative effect in binuclear zirconocenes of type **65** in comparison to the mononuclear complex **66** found a higher activity and an increased molecular weight in propene oligomerization for the mononuclear system. An electronic coupling/withdrawing effect through the phenylene bridge was invoked to explain the differences.²⁷⁸ For a related study involving mono- and dinuclear titanocene dichlorides, see ²⁷⁹.

¹ For notes concerning the industrial application, see e.g. *Chemical & Engineering News* **1996**, December 16, p. 15; August 12, p. 9-10; **1995**, October 30, p. 10; September 18, p. 17;

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Scheme and Figure Captions:

Scheme 1: Synthesis of racemic ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium ⁴⁴ or -zirconium dichloride (**7**) ⁴⁵ and its *meso*-form (Ind = indenyl). For titanium the *meso*-form is the kinetically preferred product and the *rac*-isomer had to be derived by a photoconversion reaction. With zirconium only the *rac*-form appeared to be present. With other bridged ligands, e.g. $\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{-3-R})_2^{2-}$ and R = tBu, SiMe₃, CMe₂Ph, 1-phenylcyclohexyl, *rac/meso* ratios of close to 1 are, however, obtained with zirconium as a central metal ⁴⁶ and are also subject to photoinduced interconversions.⁴⁷

Scheme 2: Possible solution equilibria of cationic metallocene catalysts obtained by protolysis with tertiary ammonium tetraarylborate (equation 5) (adapted from ref. 23b). For simplicity reactands such as NR_3 , solvent or olefin are not added to the reaction arrows; irreversible deactivation reactions are not included.

Scheme 3: General features of the Ziegler-polymerization mechanism. (a) From the inactive precatalyst the cocatalyst creates an active metal alkyl species by alkylation (if necessary) and ligand abstraction to create a vacant coordination site. (b) Repeated monomer coordination and insertion then leads to chain growth/propagation in competition with (c) chain transfer (termination) reactions to aluminum, by β -hydrogen transfer to metal or to monomer or by hydrogenolysis (if hydrogen is added as a molar mass regulator). The metal-alkyl or metal-hydride species formed from chain transfer are still active and can start a new polymerization process again.

Scheme 4: Direct-insertion mechanism according to *Cossee-Arlman* for the olefin insertion into a transition metal alkyl bond. (\square = vacant coordination site)

Scheme 5: Metathesis-mechanism according to *Green-Rooney* for the olefin insertion into a transition metal alkyl bond.

Scheme 6: Schematic representation of the suggested features for the modified *Green-Rooney* mechanism for the insertion of an olefin in a transition metal alkyl bond in Ziegler-Natta polymerization.

Scheme 7. Regiospecificity - primary (1-2) and secondary (2-1) insertion in propene polymerization; P = growing polymer chain. After a regio-irregular 2-1 insertion, polymerization can proceed via a 1-2 addition to give head-to-head insertion and sequence or the secondary alkyl ligand can isomerize to a primary ligand before the next insertion to what then becomes a 1-3 insertion.

Scheme 8. β -Hydrogen chain transfer processes involving polypropene (adapted from ref. 197).
P, P' = growing polymer chain; C* = active complex; C₃ = propene.

Scheme 9. β -Methyl chain transfer with e.g. (C₅Me₅)₂MCl₂/MAO (M = Zr, Hf)²³⁸

Figure 1. Schematic representation of possible basic ligand modifications starting from (C₅H₅)₂ZrCl₂ to control the polymer parameters. Often these modifications are employed in combination, i.e. the C₅H₅-ligands are replaced by indenyl ligands, which are tied together by a bridge to give an ansa-metallocene. The remaining hydrogen atoms on either the five- or six-membered ring of the indenyl system can be substituted further by alkyl or aryl groups (cf. section 7)

Figure 2: Proposed transition states for the hydrocyclization of *trans,trans*-1,6-*d*₂-1,5-hexadiene by a scandocene hydride, Me₂Si(C₅Me₄)₂Sc(PMe₃)H (left, cf. equation 14)¹¹⁸ as well as the hydrodimerization of (*E*)- or (*Z*)-1-deuterio-1-hexene by achiral zirconocene dichloride/MAO (right, cf. equation 15)¹¹⁹ showing the slightly preferential hydrogen instead of deuterium α -agostic interaction which then gives rise to the major products as indicated. Both reactions are viewed as models for olefin insertion into a metal-alkyl bond as encountered e.g. in metal-

catalyzed olefin polymerizations, thereby probing the validity of the "modified Green-Rooney mechanism".

Figure 3: Schematic representation of the σ -interaction of a $[\text{Cp}_2\text{MR}]^+$ fragment (viewed from the top) with incoming olefin (a). The stabilizing π -backbonding into the empty π^* -orbitals of the olefin (b) is not possible due to lack of electrons in a d^0 system.

Figure 4. Selected snapshots of the ethene insertion into the Zr-Me bond of $[\text{Cp}_2\text{ZrMe}]^+$ according to MO-calculations¹²⁷ with bond lengths (in Å) and angles (in degree).

Figure 5. Activity profiles (based on ethene uptake over time at constant ethene pressure) in the ethene polymerization with three zirconocene complexes activated with MAO at a higher (top) and lower (bottom) zirconium concentration (adapted from ref. 81). [**1** = $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$, **2** = $(\text{C}_5\text{HMe}_4)(\text{C}_5\text{H}_5)\text{ZrCl}_2/\text{MAO}$, **3** = $(\text{C}_5\text{HMe}_4)_2\text{ZrCl}_2/\text{MAO}$] The overlapping curves of the activity profiles and the resulting similar activities for the complexes at the "high" zirconocene concentration of 10^{-5} mol/l are due to the rapid polyethene precipitation at these conditions. The corresponding activity profiles at the low concentration of $2.5 \cdot 10^{-7}$ mol/l show a more constant ethene consumption. The smaller amount of polyethene produced under these conditions ensures the existence of a homogeneous phase over an extended time period. Note that with the lowering of the zirconocene concentration, the Al/Zr ratio had to be increased considerably to offset a higher degree of dissociation upon dilution of the catalytically active zirconocene-MAO complex.

Figure 6. Correlation between ethene polymerization activity and the coordination gap aperture (cga) for different methyl-substituted zirconocenes (adapted from ref. 81). The coordination gap

aperture (left) is a geometric parameter which is defined as "the largest possible angle spanned by those planes two planes through the metal center which touch the inner van der Waals outline of each of the C₅-ring ligands".¹⁵⁶ For a practical determination of the coordination gap aperture also for unsymmetrically substituted ligands, such as C₅HMe₄ see ref. 81. [**1** = (C₅H₅)₂ZrCl₂, **2** = (C₅HMe₄)(C₅H₅)ZrCl₂, **3** = (C₅HMe₄)₂ZrCl₂, **4** = (C₄Me₄P)(C₅H₅)ZrCl₂, **5** = (C₄Me₄P)₂ZrCl₂, **6** = (C₅Me₅)(C₅H₅)ZrCl₂, **7** = (C₅Me₅)₂ZrCl₂, each activated with MAO under identical conditions]

Figure 7. Schematic illustration of (a) isotactic polypropene (PP) with all methyl groups on the same side of the carbon chain back bone; (b) syndiotactic PP with the methyl groups alternating and (c) atactic PP with an irregular, statistic methyl distribution. At the right side the usual short-hand notation is given. Note that these variations in microstructure are general for vinylpolymers. Also, for pedagogic reasons the polymer is drawn here as a stretched chain whereas in reality a helical structure exists, with equal amounts of right- and left-handed helices in the lattice.¹⁹⁰

Figure 8. Correlation between the pre-catalyst and PP-microstructure, illustrating the different degree of stereochemical control. References: (a)¹⁹¹, (b)^{163,164}, (c)⁴³, (d)¹⁷⁹, (e)¹⁶⁷, (f)^{180,182}. The term hemiisotactic means that the insertion of every second (even) propene unit is sterically controlled while the intermediate (odd) insertions occur statistically.

Figure 9. ¹³C NMR spectrum (50.3 MHz) of the methyl pentad region for atactic polypropene obtained with (C₅Me₅)(C₅H₅)ZrCl₂/MAO at -30 °C, together with the assignment of the nine bands to the ten unique pentad steric arrangements. Note the three groups of signals belonging to the mm, mr and rr centered pentad (spectrum adapted from ref. 43).

Figure 10. ^{13}C NMR spectrum (50.3 MHz) of the methyl pentad region for atactic PP (top) and for polypropene obtained with $(\text{C}_5\text{H}_5)_2\text{TiPh}_2/\text{MAO}$ at $-45\text{ }^\circ\text{C}$ (bottom), together with the assignment (spectra adapted from ref. 43).

Figure 11. Model of the active complex for one enantiomeric form of the isospecific, C_2 -symmetrical metallocene $\text{C}_2\text{H}_4(\text{Ind})_2\text{ZrCl}_2$ with the two possible prochiral positions (**a** and **b**) of the 1,2-coordinated propene molecule. Position **a** is the energetically favored one. The steric demand of the indenyl ligand forces the growing chain and the propene methyl group into an orientation in the fourth and second quadrant, respectively, so that a meso (*m*) stereosequences results (**c**). The disfavored insertion from position **b** then leads to a stereoerror, a racemic stereosequence (**d**). Because of the enantiomorphous site control of the catalyst this error can be corrected upon the next insertion (**d**→**e**). Note that the respective next insertion step starts with chain and monomer having exchanged positions with each other. In reality the chain flip between "left and right" involves only a small relative motion between chain end and metallocene.

Figure 12. Principle of isotactic-atactic stereoblock polypropene formation by oscillating catalysts.

Figure 13: Principle of syndiotactic propagation with a C_s -symmetric metallocene catalyst (here $\text{Me}_2\text{C}(\text{Fluo})(\text{C}_5\text{H}_5)\text{ZrCl}_2/\text{MAO}$).^{180,182} The chain or metal moiety swings back and forth upon olefin insertion and the olefin approaches from alternating sides (as already illustrated for the isotactic insertion, cf. Figure 11), but the steric demand of the fluorenyl ligand forces the growing chain and the propene methyl group into an orientation in the first and second

quadrant, respectively, so that a racemic (*r*) stereosequences result. In reality the chain flip between "left and right" involves only a small relative motion between chain end and metallocene.

Figure 14. Indenyl-torsional conformations for the $C_2H_4(Ind)_2ZrCl_2$ complex ($ZrCl_2$ is omitted for clarity) with the notation used in the literature.²¹⁰

Figure 15. Polycyclopentene micro structures