METALLOCENE CATALYSTS

1. Introduction

The term “metallocene” refers to compounds that have a metal atom bound to two cyclopentadienide anions in a π- or pentahapto/η^5-mode. The cyclopentadienyl rings can coordinate in a coplanar (parallel) or bent fashion to the metal center. Besides the two cyclopentadienyl rings, the metal can have additional ligands depending on its valence state (Fig. 1) (1).

The cyclopentadienyl ring can be modified in many ways by substituting the hydrogen atoms through alkyl or aryl groups or anellated rings (or a combination thereof) (1,2). Furthermore, a C−H group can be replaced by an isoelectronic nitrogen (3) or phosphorus atom (4–6) (Fig. 2). The unspecified term *cyclopentadienyl ligands* (Cp) or *cyclopentadienylmetal complexes* is meant here to include substituted derivatives of the C_5H_5 parent ligand, such as C_5R_5 and also the indenyl (Ind) and fluorenyl (Flu) 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 C_5H_5 or $(C_5H_5)_mML_n$, respectively.

The term “metallocene catalyst” typically refers to the bent metallocenes of Group 4 (IVB) transition metals titanium, zirconium, and hafnium. In particular, “metallocene catalysts” refer to zirconocene complexes that are in the center of academic and industrial attention. The titanocene catalysts are unstable at conventional polymerization temperatures, the hafnium systems are too expensive. From the beginning of the 1990s, these bis(cyclopentadienyl) Group 4 IVB metal complexes (single-site catalysts) were introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins (7–14). Ziegler-Natta catalysis means the rapid polymerization of ethene and α-olefins with the aid and in the coordination sphere of a metal-containing catalyst, operating at low pressures (up to 30 bar) and low temperatures ($<120^\circ$C).

Note that the metallocenes $(C_5H_5)_2Nb^{IV}Cl_2$ and $(C_5H_5)_2Nb^{V}Cl_3$ were tested in combination with MAO (see the section Methylalumoxane—Characteristics and Function) toward ethene polymerization but did not exhibit a significant activity (15).

A noteworthy other metallocene compound used in industrial olefin polymerization is chromocene, $(\eta^5\text{-}C_5H_5)_2Cr$. The surface reaction of chromocene with silica (Fig. 3) generates a highly active catalyst for the coordination polymerization of ethene, known as the Union Carbide catalyst. This catalyst does not need any cocatalysts. At low pressure, linear polymers with a narrow molar mass distribution are obtained. In contrast to the zirconocene polymerization catalysts the metallocene moiety Cp_2M, however, does not remain intact upon reaction of chromocene with the silica surface. The nature of the active species is not fully known but at least one cyclopentadienyl ring is lost to give a surface bound cyclopentadienylchromium fragment (so-called half-sandwich complex) (Fig. 3) (16).

Group 3 (IIIB) and lanthanoide metallocene catalysts: Neutral Group 3 (IIIB) (Sc, Y, La) and lanthanoide metallocene complexes of the general type

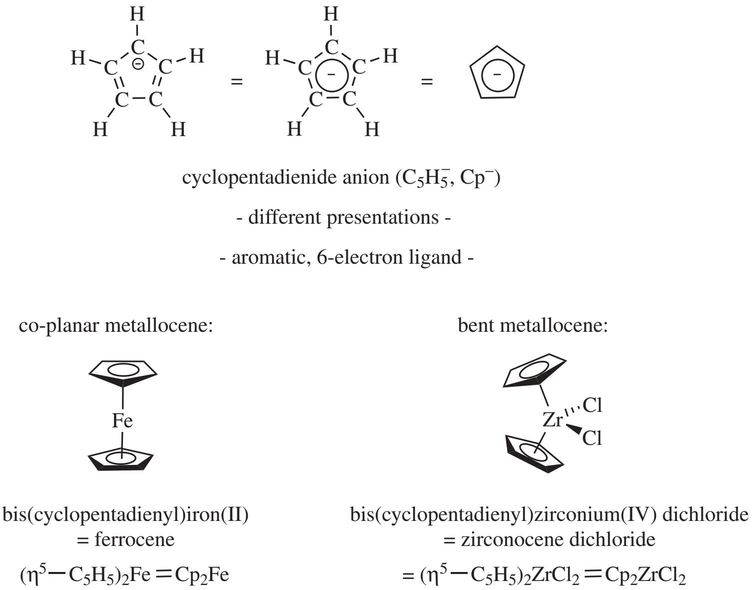


Fig. 1. Introduction to metallocenes and their nomenclature.

Cp_2MR (17) and $[Cp_2MH]_2$ (18) are also capable of polymerizing ethene. They are polymerization active even in the absence of a cocatalyst. In their monomeric form, the Group 3 (IIIB) and lanthanoide metallocenes are iso-d-electronic (d^0, not counting the *f* electrons) with the active Group 4 (IVB) metallocene cation $[Cp_2ZrR]^+$ (see the section The Borane Activators or Cationic Catalysts).

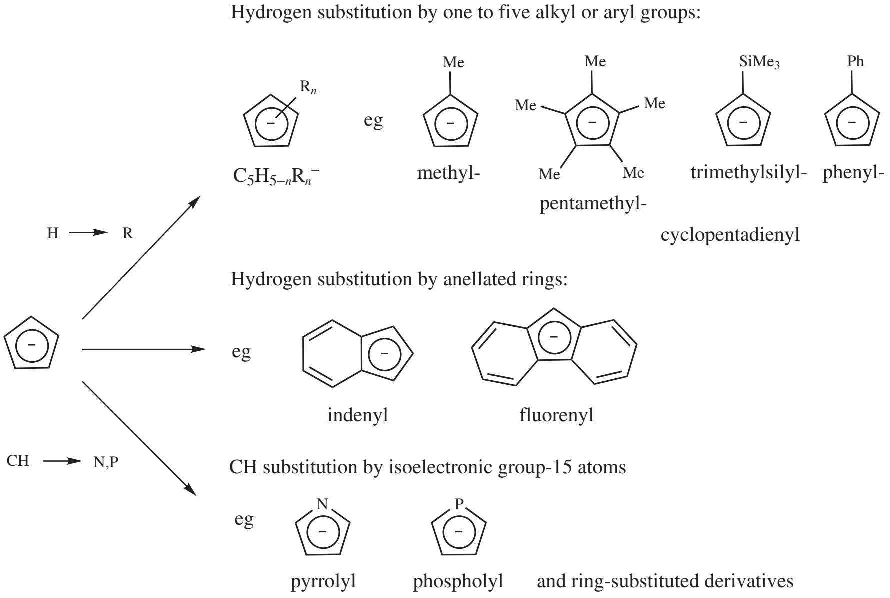
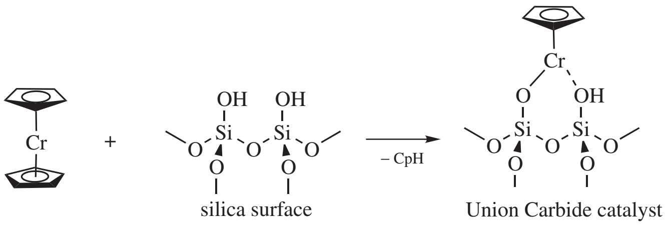


Fig. 2. Examples of modifications of the cyclopentadienyl ring.



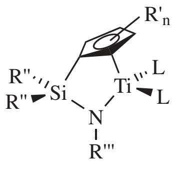
bis(cyclopentadienyl)chromium(II)
= chromocene $=(\eta^5-C_5H_5)_2Cr$

Fig. 3. Surface reaction of chromocene with silica to generate the Union Carbide complex (suggested active species).

Group 3 (IIIB) and lanthanoide metallocene catalysts show the same mechanistic features (see the section General Mechanism of Chain Growth and Chain Transfer), 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 (19) as well as *ansa*-$Cp_2Sm(thf)_2$ (thf=tetrahytetrahydrofenon) (20). A single-component chiral organoyttrium *ansa*-metallocene catalyst $[Me_2Si(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}t\text{-}(Bu)_2YH]_2$ was found to slowly polymerize propene (97% isotactic), 1-butene, 1-pentene, and 1-hexene (21). Group 3 (IIIB) and lanthanoide metallocenes, eg, $(C_5Me_5)_2LnMe(thf)$ (Ln = Y, Sm, Yb), $\{(C_5Me_5)_2SmH\}_2$, and $(C_5H_4Me)_2Yb(dme)$ 1,2-dimethoxyethane, are also used as initiators for the polymerization of polar monomers such as alkyl acrylates to give high molecular weight polymers with extremely narrow molar mass distribution (22).

Also included under the term "metallocene catalysts", albeit not adhering to the definition of a metallocene, are complexes with the cyclopentadienylsilylamido ligand (Fig. 4). These $R_2Si(Cp)(NR)ML_2$ complexes are also known as "constrained geometry" or "Dow catalysts" (23). These complexes in combination with MAO or borates (the section Cocatalysts) give rise to long-chain branching in ethene polymerization through the reinsertion of vinyl-terminated short-chain oligomers from β-hydrogen elimination. They have also been used in ethene/1-octene copolymerization (the section Copolymerization) (24) and in styrene polymerization (25,26).

The development of Group 4 (IVB) metallocenes as practical polymerization catalysts is the first large-scale industrial application for the long known and well-developed class of metallocene complexes (1). The key aspect, which earned the metallocenes their enormous academic and industrial research input (for reviews see 27–42), is that these catalysts make polymers accessible that cannot



L = Cl, Me

$CpR'_n = C_5Me_4$, substituted indenyl, fluorenyl

$R'' = Me$

$R''' = {}^tBu$, Ph

Fig. 4. Constrained geometry (pre-)catalyst.

be produced by conventional Ziegler-Natta catalysts (see the section Industrial Perspectives).

The novelty of Group 4 (IVB) 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 (43,44). Metallocene catalysts are sometimes also termed "homogeneous" refering 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 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 (see the section Heterogenization of Metallocene Catalysts) (14,32,33,45,46). 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 (1b,47,48).

2. Industrial Perspectives

Polyolefins from metallocenes (36,37) are currently introduced in the higher priced specialty markets. It remains to be seen if metallocene polyolefins can penetrate the broad array of polyolefins high volume and commodity markets. At present (2002) the market share of metallocene polymers amounts only to 2–3% (49), with metallocene linear low density polyethene (mLLDPE) having captured nearly 7% of the world's total LLDPE market (50). One of the major uses of metallocene catalyst systems at present appears to be the production of mLLDPE (9,12,51–54). The reason for the still low market share are economics and processability (55). Metallocene polymers are somewhat more expensive due to the MAO cocatalyst (see below). Metallocene polymers have to achieve similar processing characteristics on, eg, extruder lines as the polymer they should replace (9,52,53). Yet, new markets are expected to be created with the development of new classes of polyolefin polymers that are not possible with classical Ziegler-Natta technologies. Metallocene polyethene (mPE) consumption is expected to grow at rates >25% annually over the next years. North America is the leading consuming region for mPE with nearly 42% of the global consumption. Non-food packaging film markets consume the largest amount of mPE. However, food packaging film markets are projected to grow at the highest rates. Stretch wrap and food lamination films are the largest mPE consuming applications (50).

2.1. Differences between Classical Ziegler-Natta Catalysts and Metallocene Catalysts. Classical Ziegler-Natta catalysts (10,30) have several

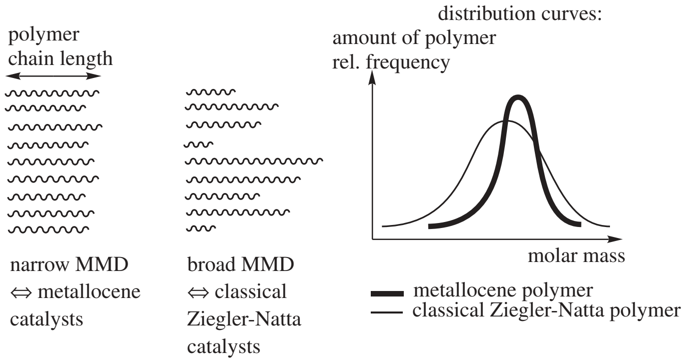


Fig. 5. Schematic representation of a narrow and broad molar mass distribution (MMD).

chemically different active metal sites. This leads to less uniform polymers, ie, a higher molar mass, composition, and tacticity distribution (see the section Polyolefin Improvements with Metallocene Catalysts, Figs. 5 and 6).

Metallocene catalysts (10,30) have essentially a single type of active metal site. This gives a “single”, more uniform type of polymer chain, ie, lower molar mass, more uniform composition (eg, branching, comonomer content), and tacticity distribution (see the section Polyolefin Improvements with Metallocene Catalysts, Figs. 5 and 6). Allow for a high versatility with countless variations through the ligand system (Fig. 2, Fig. 7, the section Propene Homopolymerization).

2.2. Advantages–Disadvantages of Metallocene Catalysts. Advantages (10) are

- A single type of catalytic site producing a polymer with narrow molar mass, composition (comonomer), and tacticity distribution (see the section Polyolefin Improvements with Metallocene Catalysts, Figs. 5 and 6).
- The versatility of the metallocene structure to allow for a greater range of polyolefin types.
- The precise control over the molecular architecture of the catalyst for highly tailored polymers (the section Control of Polypropene Microstructure, Fig. 7).

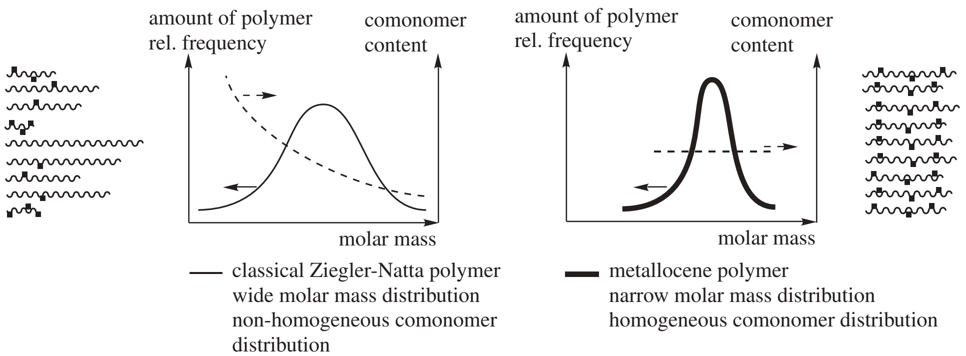


Fig. 6. Schematic representation of a more or less uniform comonomer distribution.

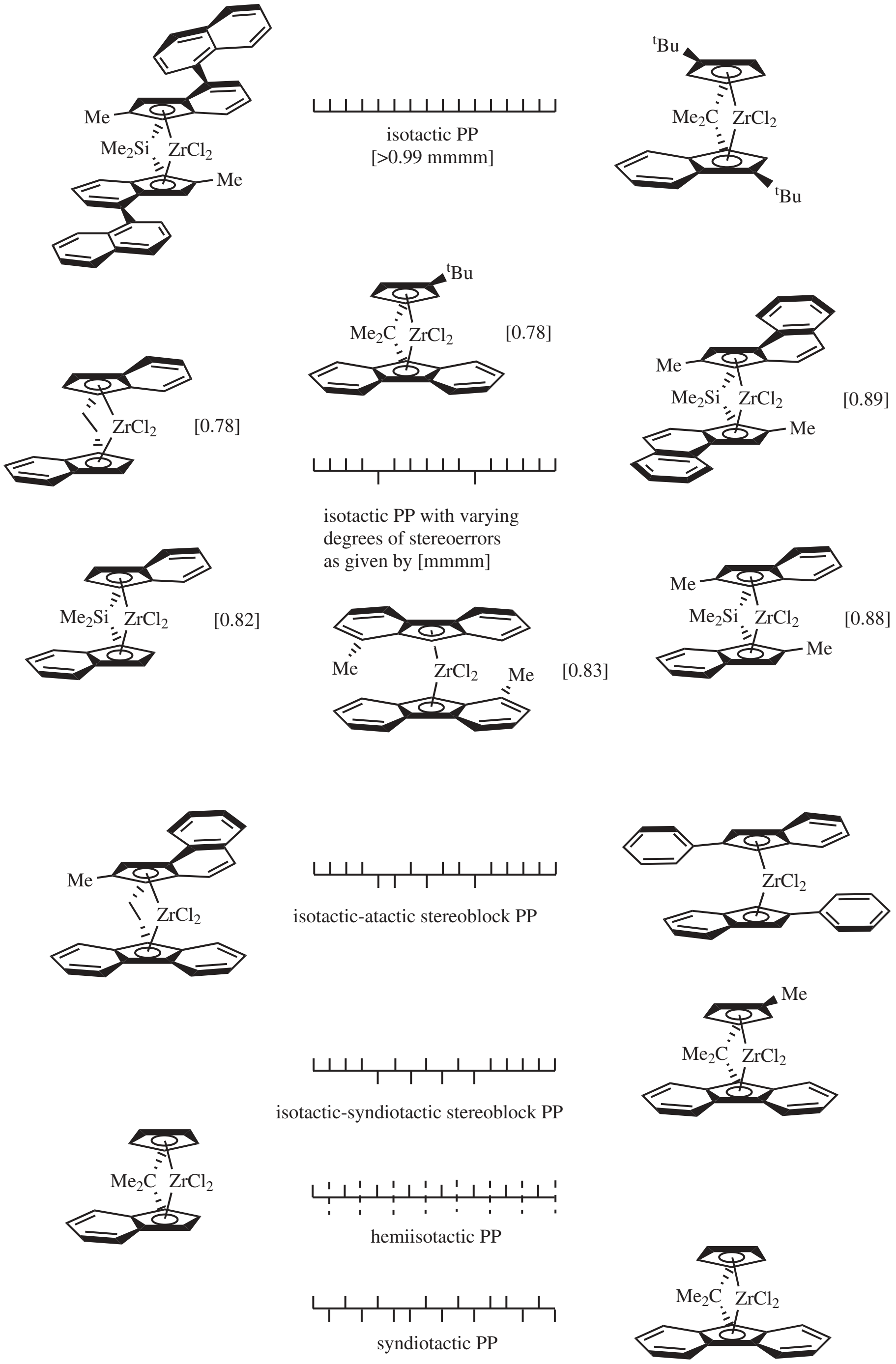


Fig. 7. Examples for a correlation between the metallocene precatalyst and the PP microstructure (comb notation, see Fig. 8) to illustrate the control over the different degrees of PP stereochemistry (30). Further information on the complexes is given in the section Propene Homopolymerization.

- Polyolefin products with new and favorable properties (see the section Polyolefin Improvements with Metallocene Catalysts).
- High activity.

Disadvantages (10) are

- The high amount of MAO cocatalyst.

The major disadvantage of metallocene catalysts are the extremely high molar Al-to-transition-metal ratios (Al/M) of between 1000 and 15,000:1 that are required to achieve the high activities. Such ratios are commercially unacceptable in terms of cocatalyst residues in polymers and costs (54). Classical Ziegler-Natta catalysts require Al/M ratios of 50–200:1. For the industrially silica-supported metallocene catalysts much less MAO is already needed, however, with Al/Zr ratios ~200–300:1 (the section Heterogenization of Metallocene Catalysts). The cost is mainly brought about through the manufacturing of both the trimethylaluminum (TMA) and its hydrolysis to methylalumoxane. The TMA is not accessible by hydroalumination (Ziegler direct-synthesis, "three-for-two process") but has to be made from aluminum metal and methyl chloride via aluminum sesquichloride, $Me_3Al_2Cl_3$, and reduction by sodium metal. Because of its high activity the metallocene component is not viewed as the significant cost factor by industry. Further information on MAO and other activators is given in the section Cocatalysts.

2.3. Polyolefin Improvements with Metallocene Catalysts.

Metallocene catalysts allow to produce consistent, controllable molecular polymer structures that can be designed to improved toughness, provide excellent impact resistance, reduced haze, better clarity, etc (8–10,51,56–58). A key feature of metallocene-catalyzed polymers that differ from conventional polyolefins is structural uniformity. This feature (a) eliminates very low and very high molar mass polymer fractions present with classical Ziegler-Natta catalysts (Fig. 5), (b) leads to uniform amounts of comonomers and their statistical distribution (Fig. 6), and (c) results in a narrow tacticity distribution.

(*a*) Narrow molar mass distribution (MMD). MMD refers to the breadth of variation in chain lengths in a polymer.

For polyethene, a narrow MMD means improved toughness, puncture, tensile, tear, and impact performance (9,51,52,56–58). For example, tougher LLDPE made with metallocene processes can be used to make thinner plastic bags with the same strength as before. A broader MMD is, however, not necessarily only negative as it favors processability, melt strength etc. For polypropene (PP) a narrow MMD improves processability in fiber extrusion processes and resin cleanliness. PP with narrow MMD is harder, more crystalline, and more transparent. Also, the polymers can be recycled more often without losing toughness (10).

(*b*) Narrow composition distribution. Metallocene catalysts yield polymer chains with uniform amounts of comonomer and a statistical comonomer distribution. Classical Ziegler-Natta catalysts give polymers where the comonomer content is concentrated in shorter chains (Fig. 6).

Polymers with uniform amounts and distribution of comonomer give improved optical properties, ie, better clarity and less haze. Also, they show improved sealing performance and lower seal initiation temperature versus conventional polyolefins (10,57).

(*c*) Narrow tacticity distribution. Isotactic polypropene made with classical Ziegler-Natta catalysts still has some atactic fractions. The presence of atactic PP fractions reduces stiffness, heat distortion temperature, and cleanliness. The absence of atactic PP in metallocene isotactic polypropene means higher stiffness, higher use temperature, and lower extractable content (10,59).

2.4. Control of Polypropene Microstructure. Changes in the steric ligand situation allow for an unprecedented control of the polymer microstructure (30,31). Besides the iso- and atactic mode, other polypropene microstructures, such as isotactic with varying degree of stereoerrors, isotactic–atactic–stereoblock, isotactic–syndiotactic stereoblock, hemiisotactic and especially syndiotactic PP can be obtained as well, with appropriate ligand modification (Fig. 7, see the section Propene Homopolymerization). The microstructure can also be greatly affected by temperature.

The different forms of homopolypropenes have different mechanical properties (without the addition of comonomer) ranging from plastic to elastic PP with decreasing stereoselectivity. The mechanical properties of different polypropenes and other poly-α-olefins strongly depend on their microstructure, which is determined by the regio- and stereoselectivity of the catalyst. 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 (10,14,58,59).

Microstructure analysis of vinyl polymers can be done by ^{13}C nmr spectroscopy (31,60–62). For polypropene the methyl region is usually used. Spectrometers >200 MHz (^{1}H, respectively, 50 MHz for ^{13}C) allow at least for the observation of pentad regions, ie, 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 ^{13}C nmr characterization meanwhile allowed for the expansion from the pentad to the heptad/nonad levels in the methyl region and to the octad/decad levels in the methylene region (63). A special nmr notation is used here for the relative configuration of neighboring centers in vinyl polymers (64). If the pseudo-asymmetric tertiary methine carbon atoms of two neighboring monomer units have the same configuration it is called a *meso* (*m*) diad, if they are of opposite configuration it is a *racemic* (*r*) diad (Fig. 8). The nmr notation for ideal isotactic PP would then be "… *mmmmmm* …" for ideal syndiotactic PP "… *rrrrrr* …". A spectrum of atactic polypropene features roughly nine bands corresponding to the ten unique steric arrangements of five adjacent monomer units (*mmmm, mmmr, rmmr, mmrr, mmrm and rmrr overlap, mrmr, mrrm, rrrm, rrrr*). 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 nmr is useful not only in the determination of steric sequence distributions but also in the detection of end groups (65) (see the section Chain-Transfer

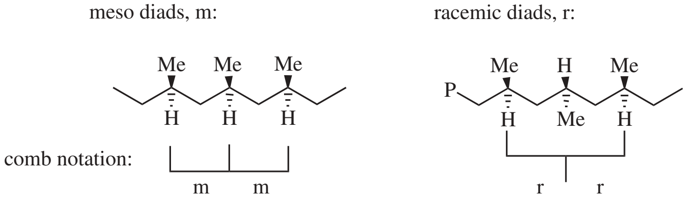


Fig. 8. Schematic representation of meso- and racemic diads as microstructures of vinyl polymers.

Processes) and structural defects such as regiochemical insertion errors (66) (the section Regioselectivity in α-Olefin Insertion) if they are present in amounts >1%.

2.5. Heterogenization of Metallocene Catalysts. Current polymerization technology is based on gas-phase and slurry processes (67). The established Ziegler-Natta catalysts are all heterogeneous, hence it is necessary to also heterogenize metallocene catalysts for industrial applications. Thus, metallocene catalysts have to be fixed on a carrier or support to be used as "drop-in" catalysts in existing plants (32,33,38,45,46,68). The pure metallocene precursor is not suitable for technical applications since their use in conventional gas-phase or slurry reactors would cause the formation of polyolefin deposits on the reactor walls (known as "fouling"). A continuous process would not be possible with homogeneous, solution-based metallocene catalysts (46). The carrier also functions as a template for the polymer morphology so that free flowing powders are obtained, thereby preventing wall deposits of the polymer. The obtained polymer particles represent a replica of the shape of the support with an increase in size. Fragmentation of the support is a prerequisite for the particle growth and the simultaneous conservation of morphology. Carriers (46) can be inorganic support materials as (wet) silica (gel) (33,45,69), alumina, or zeolites or organic support materials as cyclodextrins or polymers such as cross-linked polystyrene (70,71) or poly(organosiloxanes) (72). The polymerization process of silica-supported metallocene/MAO catalyst systems was followed by scanning electron micrography (SEM) (33,45,68).

Common methods of immobilizing the catalyst involve first heterogenization of the cocatalyst. The support can be treated either with methylalumoxane (or methylaluminoxane) MAO or with trimethylaluminum. The latter may be followed by addition of water to generate MAO if the carrier, such as wet silica does not already contain water (see below). This cocatalyst-modified carrier is then mixed with the catalyst precursor and may subsequently be activated further by additional trialkylaluminum or MAO. The fixation of MAO or TMA can be due to an absorption process or by chemical bonds from the reaction with surface hydroxyl, eg, in the case of silica. The metallocene catalyst precursor is usually immobilized by absorption within the primary MAO layer. The metallocene may, however, also be bonded through the reaction of surface Si−OH groups with Cl−Si in the bridge or ligand periphery. Heterogenation is mostly carried out in slurry but can also be done in gas-phase processes (33,38,45,46,68).

Metallocene complexes that contain α-olefinic side groups on the ligand can be simultaneously incorporated into a growing polyethene chain as a comonomer upon activation in an ethene solution polymerization process. As a consequence the active, homogeneous metallocene/MAO moiety is transferred to the hetereogeneous polymer precipitate where it is available for further use. The formation of its own support by the metallocene catalyst in a polymerization process is also termed "self-immobilization" (46).

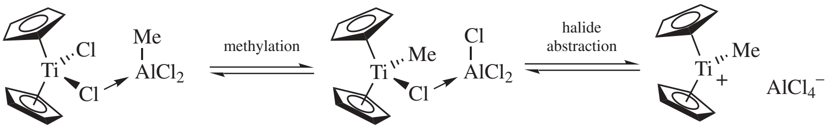
The above-mentioned treatment of a support by TMA appears to be a more universal method for creating a heterogeneously effective and highly active cocatalyst. As carrier materials SiO_2, AlF_3, B_2O_3, starch, cellulose, active carbon, polyethene, polypropene, polystyrene, etc, have been used. The carier material is reacted with TMA in toluene to block all potential surface Lewis basic centers that could otherwise poison the Lewis acidic metallocenium catalyst. The subsequent addition of a calculated amount of water gives a heterogeneous partially hydrolyzed trimethylaluminum (PHT). The PHT analyses different from common MAO. PHT also appears to lead to higher activities, ie, compensates for the usual loss in activity upon metallocene immobilization (73).

A clear advantage of heterogenized metallocene/MAO catalysts is the significant decrease in the necessary excess of MAO that leads to a strong decrease in catalyst costs. For the industrially silica-supported metallocene catalysts the Al(MAO)/Zr ratios are $\sim$200–300:1 (45,74). Which is explained by the spatial fixation of MAO in the vicinity of the metallocene (68). As a disadvantage of the catalyst immobilization or heterogenization, a marked drop in activity when compared to the solution behavior can be noted, as the metal centers may become less accessible for the monomer approach (45,46). Also, a metallocene catalyst may change its stereoselectivity. The catalyst $Me_2C(C_5H_4)$ (Flu′)$ZrCl_2$/MAO gives syndiotactic polypropene in solution polymerizations, yet changes to isotactic when supported. The immobilization and steric demand of the support apparently no longer permits the chain flip, ie, inversion of the active site/monomer approach. The polymerization mechanism changes from a chain migratory to a chain stationary insertion (the section Stereoselectivity in α-Olefin Insertion, Fig. 15, the section C_s-symmetric Bridged Metallocenes, Fig. 17) (46,75).

3. Historical Development

Group 4 (IVB) metallocene catalysts for the polymerization of ethene are almost as old as Ziegler-Natta catalysis itself. In 1957, a soluble, crystalline, and isolable complex from $(C_5H_5)_2TiCl_2$ and $AlEt_3$ was reported that was polymerization active toward ethene (76–78). However, the catalyst activity was much lower than that of a comparative heterogeneous Ziegler catalyst, eg, $TiCl_4/AlEt_3$, although it was already noted that traces of oxygen in the monomer increased the metallocene catalyst activity (77). The $(C_5H_5)_2TiCl_2$ complex alone is completely inactive toward ethene polymerization. The value of these titanocene dichloride/aluminum alkyl "bimetal complexes" for mechanistic studies of the heterogeneous Ziegler catalysts was quickly recognized (79). The $(C_5H_5)_2TiCl_2$ complex with different alkylaluminium halide cocatalysts ($AlMe_2Cl$, $AlEt_2Cl$, $AlEtCl_2$) was used as a model system to develop an understanding of the classical Ziegler catalysis because of its well-defined character and the low polymerization activity. Important ideas for the mechanism of Ziegler-type polymerization reactions were derived therefrom, namely, having electron-deficient compounds as catalysts (80), mechanistic suggestions for Ti alkylation, activation equilibria, Ti-olefin π-complex formation, chain growth at titanium and Ti → Al chain-transfer processes were based on kinetic studies (81).

The very important suggestion that the catalytic activity of Group 4 (IVB) 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, eg, as in equation 1 via methylation and halide abstraction, was based on electrodialysis studies of the $(C_5H_5)_2TiCl_2/AlMe_2Cl$ system (82). These early ingenious findings were later proven correct by the independent isolation of catalytically active zirconocenium cations with noncoordinating borate anions (see the section Borane Activators or Cationic Catalysts). The 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 that was active toward ethene polymerization (83).



(1)

In 1973 and 1975, two research groups (84,85) noted a strong polymerization rate increase when small amounts of water where added to $(C_5H_5)_2TiEtCl/AlEtCl_2$ and $(C_5H_5)_2TiCl_2/AlMe_2Cl$, respectively. No conclusive explanation for this effect was given, however. These findings were unusual as water was, so far, generally viewed as a catalyst poison for Ziegler systems and perhaps only used to lower the molar mass of polymers (85).

Until then, 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, and co-workers (86) could, however, show that a chlorine-free system based on $(C_5H_5)_2TiMe_2$ and $AlMe_3$ became highly active toward ethene polymerization, when water had been added to the aluminum alkyl before reaction with the metallocene. The optimum Al to H_2O ratio lay between 2:1 and 5:1 and the formation of alumoxanes (see the section Methylalumoxane—Characterization and Function) was assumed. No activity was found at a ratio of 1:3 when all three alkyl groups were hydrolyzed. It was also shown that zirconocene complexes could be activated for ethene polymerization. Eventually in 1980, MAO was synthesized separately and employed as an activator for $(C_5H_5)_2ZrMe_2$ or $(C_5H_5)_2ZrCl_2$ to give record high activities of the order of 10^6 g PE/(g Zr · h · bar) (87–90). 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 (91). Industrial interest was awakened, but the simple, achiral metallocenes did not *polymerize* propene (at least not under normal conditions, see the section Propene Homopolymerization and Olefin Oligomerization), but gave only atactic polypropene of low molar mass (5,62,89,92).

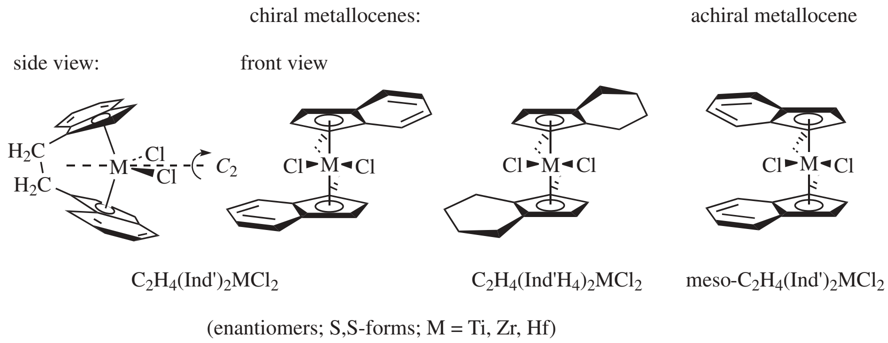


Fig. 9. Examples of typical chiral ansa-metallocenes for stereoselective propene polymerization (Ind = indenyl) in comparison to the related, also possible achiral meso-form. For the synthesis, see (93,94). The position of the C_2-axis is indicated in the side view of $C_2H_4(Ind')_2MCl_2$.

Research by Brintzinger and co-workers in the early 1980s introduced the chiral bis(indenyl)- and bis(tetrahydroindenyl)metallocene compounds, $C_2H_4(Ind')_2MCl_2$ and $C_2H_4(Ind'H_4)_2MCl_2$ (M = Ti, Zr) (Fig. 9) (93,94). The way chosen here [out of other possibilities, see the section Propene Homopolymerization (2,95)] to incorporate chirality in these metallocenes, is freezing the rotation of the substituted cyclopentadienyl rings by tying them together with a handle, eg, an ethanediyl bridge. By using the Latin word for bent handle "*ansa*", this type of metallocene is also called *ansa*-metallocene (96). Note that a C_2-axis of rotation is still present in the enantiomeric forms of $C_2H_4(Ind')_2MCl_2$ and $C_2H_4(Ind'H_4)_2MCl_2$ (M = Ti, Zr) (as well as in many other *ansa*-metallocenes), hence the systems are not asymmetric, only dissymmetric (ie, lacking mirror symmetry). This is, however, sufficient to induce the existence of enantiomeric forms (97). Moreover, the C_2-symmetry of these metallocene catalysts is important in that it reduces the number of possible competing diastereomeric transition states (97) and provides the isotactic selectivity in propene polymerization (Fig. 7, see the section Stereoselectivity in α-Olefin Insertion and Propene Homopolymerization). In 1984–1985, the first stereoselective polymerizations of propene with chiral metallocene catalyts were reported (62,98).

In 1986, cationic metallocene complexes of Group 4 (IVB) were first synthesized and shown to polymerize ethene in the absence of an aluminum cocatalyst (99,100). One-electron oxidants were used to generate the zirconocenium cations (eq. 2).

$$\begin{gathered}
Cp_2ZrR_2 + ox \longrightarrow [Cp_2ZrR]^+[BPh_4]^- + R\bullet + red \\
R = Me,\ CH_2Ph \\
ox = [(C_5H_4Me)_2Fe]^+[BPh_4]^-,\ Ag^+[BPh_4]^- \\
red = (C_5H_4Me)_2Fe,\ Ag^0
\end{gathered} \tag{2}$$

An alternative access to cationic Group 4 (IVB) metallocenes was the protonolysis of metal–alkyl bonds with tertiary ammonium-tetraphenylborate (eq. 3) (101,102).

$$\begin{array}{l} \mathrm{Cp_2MMe_2} + [\mathrm{R_3NH}][\mathrm{BAr_4}] \longrightarrow [\mathrm{Cp_2MMe}]+[\mathrm{BAr_4}]- + \mathrm{CH_4} + \mathrm{R_3N} \\ \qquad \mathrm{M = Ti, Zr} \\ \qquad \mathrm{R_3N = Ph(Me_2)N, nBu_3N} \\ \qquad \mathrm{Ar = Ph, p\text{-}C_6H_4R'\ (R' = Me, Et)} \end{array} \tag{3}$$

With the amine still present, the formation of weakly bound amine complexes may be assumed (102). This amine coordination blocks the free site for olefin coordination. Low temperature H nmr investigations could prove a fluctuating η^2-coordination of a phenyl ring from $BPh_4{}^-$ to the cationic zirconium center (103). Also, this phenyl ring coordination competes with the olefin. One of the phenyl rings in the $[BPh_4]^-$ anion could even be metalated with CH_4 elimination by an electrophilic attack of the highly electron-deficient 14-valence electron $[(C_5Me_5)_2ZrMe]^+$ cation (101). Phenyl metallation results in an irreversible deactivation reaction. Subsequently, the polymerization activity of $[Cp_2ZrMe]^+[BPh_4]^-$ was still low when compared to MAO-activated systems. To enhance the activity of the cationic metallocenium catalysts $[Cp_2ZrMe]^+$ even weaker coordinating anions had to be introduced (see the section The Borane Activators or Cationic Catalysts) (35,103).

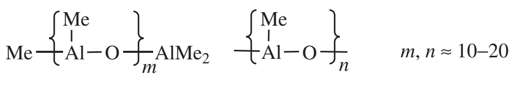
4. Cocatalysts

The zirconocene complexes are not catalytically active by themself but require the action of a cocatalyst. The cocatalyst directly associated with their application oriented development is MAO.

4.1. Methylalumoxane—Characteristics and Function. The development of metallocene catalysis for olefin polymerization is closely tied to the discovery and use of the cocatalyst MAO (104). Alumoxanes, in general, are understood as species containing an oxygen bridge between two aluminum atoms, −Al−O−Al−. Any alkyl, aryl, halide, alkoxy or other group can then be the other ligand(s) bonded to the aluminum atoms. Alumoxanes are an independently studied class of compounds, known long before the interest in the methyl derivative as a cocatalyst for zirconocenes arose (105). Alumoxanes are obtained from the controlled hydrolysis of organoaluminum compounds. For methylalumoxane the careful hydrolysis of TMA by crystal water of $CuSO_4 \cdot 5\ H_2O$, $MgCl_2 \cdot 6\ H_2O$ or $Al_2(SO_4)_3 \cdot {\sim}14{-}18\ H_2O$ proved to be the most effective laboratory method of obtaining uniform products in high yield (105–108). Technically MAO is made from the direct reaction of water/ice with TMA.

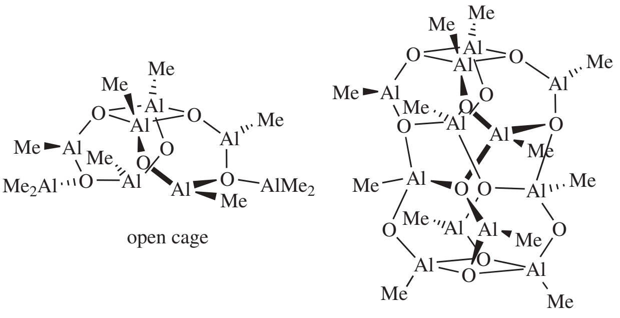
Higher alkyl alumoxanes are defined monomeric or oligomeric compounds (55), yet, methylalumoxane still remains a “black box” despite its uniqueness as a cocatalyst. Other alumoxanes, such as ethyl-, *iso*- or *tert*-butyl-alumoxane, were tried as cocatalysts but did not reach the actitvity of MAO (55,88,109,110), hence, the symbiotic relationship between metallocene catalysts and the MAO cocatalyst.

Attempts were made to elucidate the MAO structure (108,111), eg, with the help of size exclusion chromatography (112), nmr (113), mass balance, and phase-separation experiments (114). The methylalumoxane structure can,



$$\mathrm{Me}\!-\!\left[\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}\!-\!\mathrm{O}\right]_m\!\!-\mathrm{AlMe_2} \qquad \left[\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}\!-\!\mathrm{O}\right]_n \qquad m, n \approx 10\text{–}20$$

linear oligomer cyclic oligomer



open cage

closed cage

Fig. 10. Idealized structures of MAO as linear and cyclic oligomers or open and closed cage-type clusters.

however, only be postulated as being a mixture of linear or cyclic 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 have been suggested as well (Fig. 10) (115,116). Such MAO oligomer cage structures $(\mathrm{MeAlO})_n$ without and with TMA, $(\mathrm{MeAlO})_n \cdot (\mathrm{Me_3Al})_m$, and their percentage abundance have been modeled in a combined density functional theory and statistical mechanical approach. These studies found an average n of 17.2 at 298 K and 16.9 at 398 K. Also, very little TMA was calculated to be bound to MAO (117).

From its synthesis, MAO contains residual trimethylaluminum. About 5% TMA is stated in commercial MAO–toluene solutions in company certificates, although other studies suggest up to 25–50% (113,115,118) of partly free and in part "associated" (115) TMA to MAO. The TMA content is important for the solubility of MAO in aromatic hydrocarbons (112). The agreement appears to be that the MAO/TMA oligomers are fluxional molecules with a dynamic equilibrium, which changes their size and structure (45,115). The average molar mass depends on the preparative conditions (108) (~900–1100 g/mol for the commercial 10 wt % toluene solutions). Toluene solutions of MAO obviously "age" within several weeks time (55) especially when the flask is opened more often under inert gas, so that free TMA evaporates. The aging leads to gel formation and a change (usually an increase) in their cocatalytic activity when used in polymerization catalysis (119).

The full cocatalytic functionality of MAO toward zirconocenes is not known (34,110). An nmr (120) and a combined infrared (ir)/nmr study on zirconocene dichloride–MAO systems (121) or an X-ray structure of a neutral dimethylzirconocene/aluminoxane adduct $\{(\mathrm{C_5H_5})_2\mathrm{ZrMe}(\mu\text{-}\mathrm{OAlMe_2})\}_2$ (122) did not shed much light on this question. The following functions of MAO in metallocene catalysis can be assumed:

- MAO methylates the metallocene dihalide ($\mathrm{Cp_2ZrCl_2}$) to give the species $\mathrm{Cp_2ZrMeCl}$ and $\mathrm{Cp_2ZrMe_2}$.

- MAO abstracts a chloride or methide anion with the formation of a $[Cp_2ZrMe]^+$ cation and a weakly coordinating $[Cl-MAO]^-$ or $[Me-MAO]^-$ anion.
- MAO establishes a stabilizing environment for the metallocene cation or cation–anion pair in the form of a host–guest or “crown-alumoxane” complex (123).
- MAO is a scavenger for deactivating impurities in the monomer or solvent.

MAO is a better alkylating agent and has a greater capacitiy for producing and stabilizing cation-like complexes, like $[(C_5H_5)_2TiMe^+][Cl\text{-}Al(Me)O]_n^-$ than TMA (124). Zirconocene dichloride and TMA alone were found to be either inactive (114,124) or to exhibit very low polymerization activity (44,113).

The ligand abstraction in a metallocene derivative Cp_2MR_2 creates the space and metal orbital (125) necessary for the σ-interaction with the incoming olefin (see Fig. 12, the section Mechanism of Chain Growth). The formulation of metallocene cations $[Cp_2MR]^+$ as active species is based on the work of Dyachkovskii and co-workers noted above (82) and on the synthesis of isolable and olefin-polymerization active cations by independent routes (see the section The Borane Activators or Cationic Catalysts). 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 (126).

The stabilization of the metallocenium cation by MAO is akin to enzymatic catalysis where the organic hull of the enzyme protects its active center. 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) (127).

It has been found that very high ratios of MAO to metallocene are required to achieve a good polymerization activity. Many zirconocene systems described in the literature require Al/Zr ratios on the order of 1000:1–10 000 : 1 to achieve a reasonable activity in solution. This is a serious shortcoming of the MAO cocatalyst. Such ratios are commercially unacceptable in terms of the cost (54) and the amount of residues left in the polymer. Classical Ziegler-Natta systems require Al to M ratios of between 50 and 200:1. For the industrially silica-supported metallocene catalysts much less MAO is already needed, however, with Al/Zr ratios 200–300:1 (the section Heterogenization of Metallocene Catalysts).

The activity of the zirconocene–MAO catalyst often seems to increase “indefinitely” with the increase of the Al/Zr ratio (88,89,92,106). This effect is usually discussed on the assumption of an equilibrium between an inactive metallocene precursor and its catalytically active form (eq. 4) (128,129). The activation equilibrium sketched in equation 4a 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, I_1), active (C^*), and deactivated zirconocene dimers (I_2) (eq. 4b) (130). Necessary reactivation reactions from bimetallic deactivation processes and equilibria are apparently responsible for the high MAO excess.

$$Cp_2ZrMe_2 + MAO \rightleftharpoons [Cp_2ZrMe]^+ + [Me\text{-}MAO]^- \tag{4a}$$

$$2\,C^* \overset{k_1}{\rightleftharpoons} I_1 \xrightarrow{k_2} I_2 \tag{4b}$$

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. It is suggested that the catalytically active complexes C^* are deactivated in a two-step deactivation process by a reversible process followed by an irreversible reaction to form inactive species I_1 and I_2 (eq. 4b) (130b). 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 that 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 (130). 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 electron paramagnatic resonance (epr) study (131). Yet, 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 Cp_2ZrCl_2–MAO system (131).

With the *ansa*-metallocenes $C_2H_4(Ind'H_4)_2ZrCl_2$ (123), $Me_2C(C_5H_4)(Flu')ZrCl_2$, and $Me_2Si(Ind')_2ZrCl_2$ (132) a maximum activity for molar Al/Zr $\approx$ 3500, 1300, and 10,900, respectively, was reported in propene polymerization and also in ethene polymerization for the latter two with Al/Zr $\approx$ 5100 and 26,600, respectively. For propene polymerization, it was also found that the catalyst activities and polymer molecular masses depended on 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.

The necessary Al/Zr ratio also depends on the zirconocene concentration. At a 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 (6,128,133). For the record high activities reported by Kaminsky and co-workers (87,90) 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 (54).

Significant efforts are still made to reduce the amount of MAO required. Apparently, up to 90% of the MAO can be replaced by TMA without significant loss in polymerization activity toward ethene (106). 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, eg, silica (134). Until today the only proven alternative to MAO are noncoordinating borate counterions (see the section The Borane Activators or Cationic Catalysts).

Also, the search for MAO substitutes continues. A recent report highlights hydroxy isobutylalumoxane as a possible alternative (49,55).

4.2. The Borane Activators or Cationic Catalysts.

Highly Lewis-acidic perfluorinated arylboranes can be used for the generation of polymerization active zirconocenium cations (35,135). The zirconocenium cations are then stabilized by weakly or *noncoordinating* perfluorinated arylborate anions, so-called "BArF" anions (Fig. 11) (136). In a typical activation procedure the tris(pentafluorophenyl)borane, $B(C_6F_5)3$ is reacted with Cp_2ZrMe_2 to give a crystallographically characterizable, active polymerization catalyst (137). In

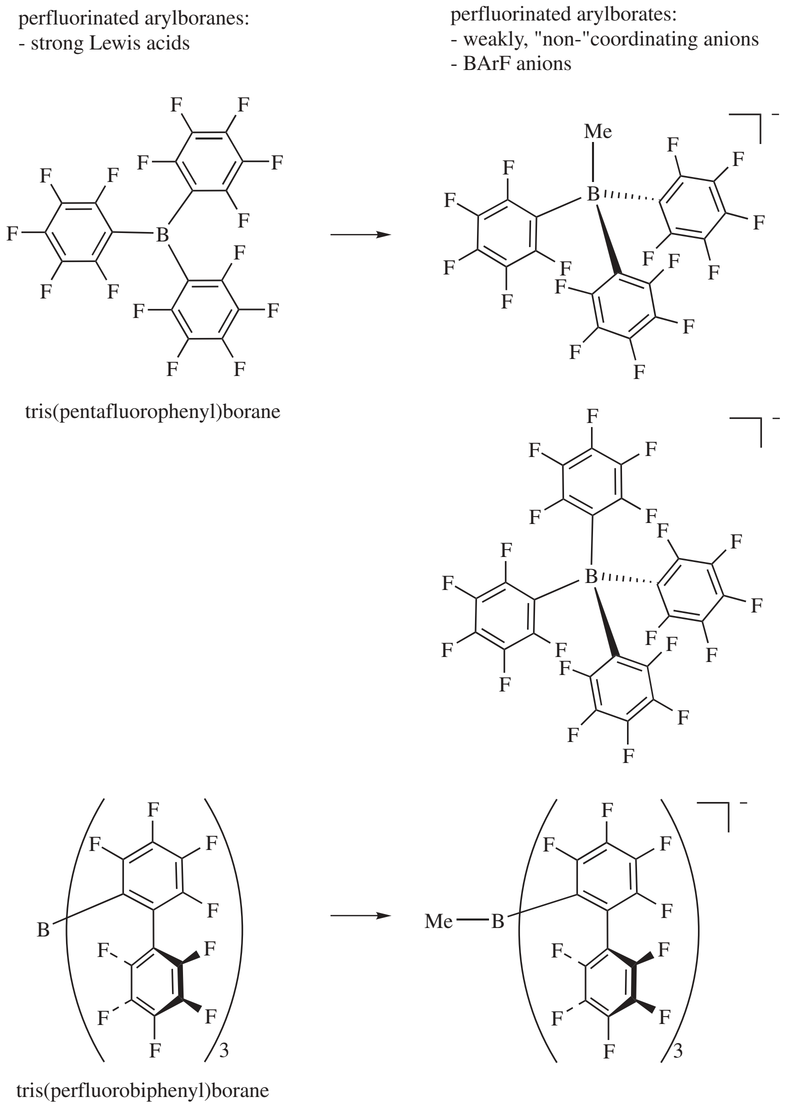
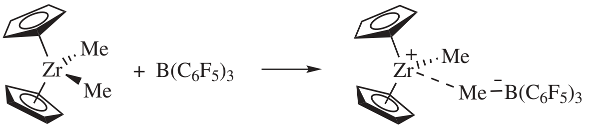


Fig. 11. Schematic drawings of perfluorinated arylboranes (as activators) and -borates (as "noncoordinating" anions) used in the generation and stabilization, respectively, of zirconocenium cations.

a side-product free reaction, the borane abstracts a methyl group from the metallocene (eq. 5) to give in the solid state a weakly coordinated cation-anion pair with a non-linear Zr(μ-Me)B bridge (138). It is suggested that a similar interaction is present in zirconocene–MAO systems (see eq. 4).



(5)

Triphenylcarbenium (trityl)-borate salts can be reacted with Cp_2ZrMe_2 in order to avoid the presence of amines (see eq. 3). The triphenylcarbenium cation abstracts a methide group, thus creating the zirconocenium cation in the presence of a tetraarylborate anion; aryl is usually pentafluorophenyl (eq. 6) (139).

$$\mathrm{Cp_2ZrMe_2 + [Ph_3C]^+[B(C_6F_5)_4]^- \longrightarrow [Cp_2ZrMe]^+[B(C_6F_5)_4]^- + Ph_3CMe} \tag{6}$$

The counterion, eg, $[B(C_6F_5)_4]^-$ versus $[MeB(C_6F_5)_3]^-$, has an effect on the activity and stereoselectivity, when chiral catalysts are used (140). From the reaction of Cp_2ZrMe_2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ dimeric complexes may also form (eq. 7) depending on temperature or the nature of the Cp-ligand (141). A dimeric complex, as described in equation 7, could also be crystallographically characterized by using the bulky tris(perfluorobiphenylborane) (Fig. 11) as an abstracting agent. The reduced coordinative tendencies of the resulting bulky borate stabilize the dimer (142).

$$\begin{aligned}&\mathrm{2\,Cp_2ZrMe_2 + [Ph_3C]^+[B(C_6F_5)_4]^- \longrightarrow}\\ &\qquad\mathrm{[Cp_2Zr(Me){-}\mu{-}Me\text{-}Zr(Me)Cp_2]^+[B(C_6F_5)_4]^- + Ph_3CMe}\end{aligned} \tag{7}$$

The very weak ion-pairing behavior of the bulky methyltris(perfluorobiphenyl)borate versus $[Me{-}B(C_6F_5)_3]^-$ lead to a significant activity enhancement with constrained geometry (Dow) catalysts (Fig. 4) toward ethene and ethene–hexene copolymerization (142).

The metallocenium–BArF–borate cation–anion contacts are weak enough so that the *non*coordinating anion can easily be displaced by the olefin. Quantitative thermodynamic and kinetic parameters for ion pair formation, dissociation and reorganization in $[Cp_2MMe]^+{-}[MeB(C_6F_5)_3]_3{}^-$ complexes (M = Zr, Hf) and other metallocenium ions in various solvents are available (35,143,144). The activity of these ionic, base-free catalysts is comparable to or even surpasses those 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 (139,145). Thus, in applications of the zirconocenium–borate catalysts, higher aluminum alkyls are favorably added to act as purifying agents and thereby enhance the observed activity (140,146). Trimethylaluminum is not suitable as a scavenger here, because of inactive heterodinuclear dimers that are formed in equilibrium with the monomeric cations (eq. 8) (141). With

$AlEt_3$ related heterodinuclear dimers form but dissociate more readily so that polymerization activities increase in the order Me < Et (147).

$$[Cp_2ZrMe]^+ + AlMe_3 \rightleftharpoons [Cp_2Zr\text{–}(\mu\text{–}Me)_2\text{–}AlMe_2]^+ \qquad (8)$$

5. General Mechanism of Chain Growth and Chain Transfer

5.1. Mechanism of Chain Growth. Olefin insertion into a transition-metal alkyl bond at a metallocene is believed to occur via a combination of the Cossee-Arlman and modified Green-Rooney mechanism (31). The direct insertion mechanism, proposed by Cossee and Arlman (148), involves a loosely coordinated four-center transition state (see Fig 12). The modified Green-Rooney mechanism (149,150) proposed an α-agostic C−H interaction in the transition state to assist the insertion of an olefin (see Fig 12). Such an α-agostic interaction in metal-catalyzed olefin polymerizations is supported by experimental evidence (151–155) and theoretical (156,15) considerations. The α-agostic interaction stabilizes (lowers the energy of) the transition state by relieving part of the electron deficiency of the 14-valence electron $[Cp_2ZrR]^+$ species. The dynamic olefin insertion process has been studied theoretically on various levels of sophistication (158), such as density functional theory (159) or by ab initio methods (160,161).

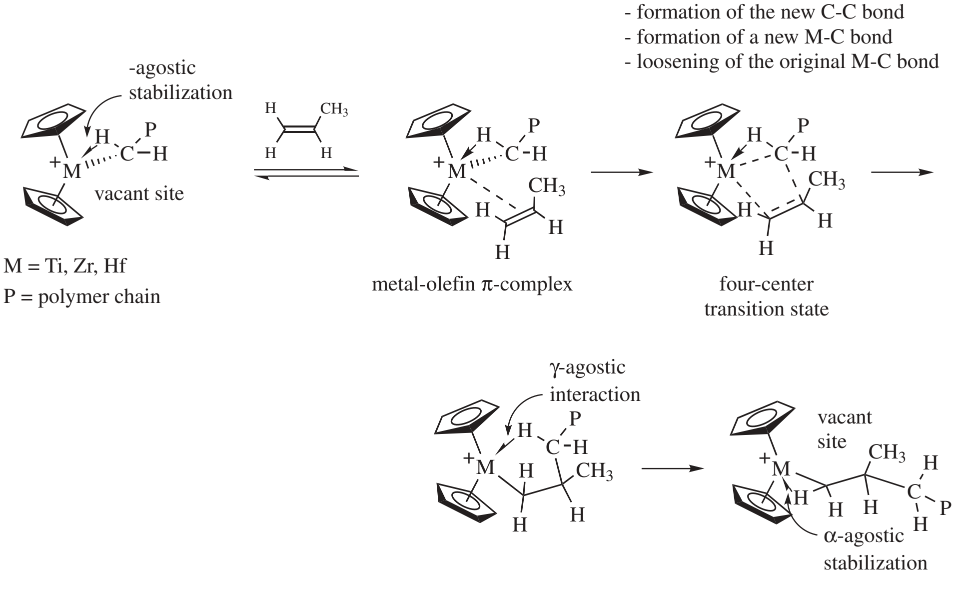


Fig. 12. Schematic representation for the olefin insertion in the transition-metal alkyl bond. Because there are no *d* electrons available for π-back-bonding from the metallocenium d_0 system into the empty π* orbitals of the olefin, the metal–olefin π-interaction is not stabilized and remains weak. The cis-positioned alkyl ligand (chain end) can then be transfered to the olefin or in other words the olefin inserts into the metal–alkyl bond. During the insertion, the initial α-agostic interaction becomes a γ-agostic C−H interaction. Resuming the α-agostic interaction regenerates a vacant site for the next momomer. Note that chain end and vacant site/direction of approach switch with each monomer added.

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* (HDC=CHMe) with $C_2H_4(Ind'H_4)_2ZrCl_2$/MAO, $Me_2Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$/MAO, or $Me_2Si(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}t\text{-}Bu)_2ZrCl_2$/MAO only slightly affects the isotacticities of the polymers formed but significant differences in the mean degree of polymerization, P_N are evident (162). The mean degree of polymerization is proportional to the number-average molar mass, M_n, and given by the ratio of the rates of polymer growth, ν_P, and chain termination, ν_T, $P_N = \nu_P/\nu_T$ (163) Polymers derived from (*E*)-propene-1-*d* have molar masses that are higher by a factor of 1.3 than those obtained from (*Z*)-propene-1-*d*. The chain growth is terminated mainly by β-H transfer from −CHMe− (the section Chain Transfer Processes), thus, ν_T will not show an isotope effect. However, if insertion of an olefin requires an α-hydrogen contact then the configuration of the α-CHD-group can affect ν_P. Due to its lower zero-point energy a transition state with a Zr←D−C(α) bond will have a lower rate of insertion than its Zr←H−C(α) counterpart (H/D isotope effect) (162).

Regioselectivity in α-Olefin Insertion. Regioselectivity 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 (163). Figure 13 illustrates that if position 1 (the CH_2-end) of propene is connected to the metal center and position 2 (the $CHCH_3$-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-Natta (164) and metallocene catalysts (135). Consecutive regio-regular insertions result in a head-to-tail enchainment. When position 2 of the olefin is linked to the metal center a "2-1" (also 2,1- or secondary) insertion follows. Regio-irregularities such as a 2-1-addition in a series of 1-2 insertion

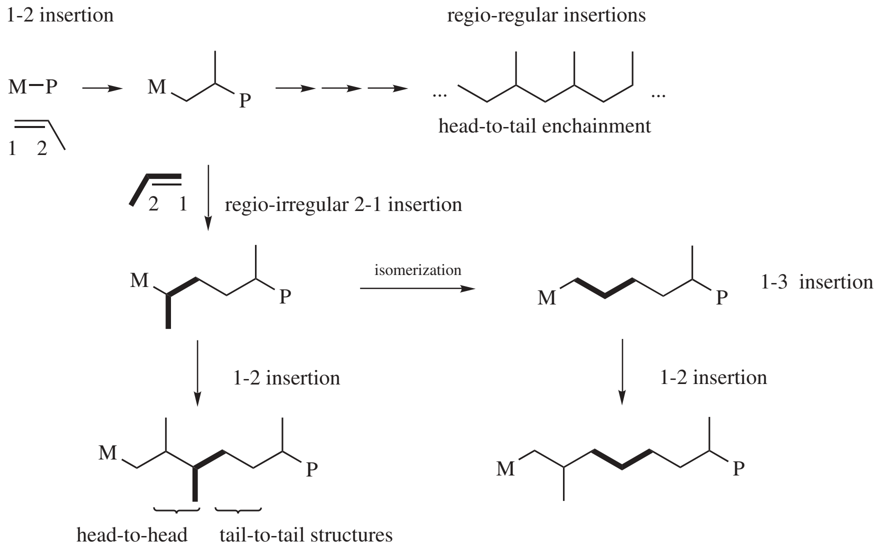


Fig. 13. Regioselectivity in propene polymerization at a transition-metal center M.

(and vice versa) than leads head-to-head and tail-to-tail structures. The secondary alkyl ligand can also isomerize to a primary ligand before the next insertion to give a 1-3 insertion. At higher temperature, isomerization or 1–3 insertion becomes more dominant and can replace all original 2–1 insertions (165) A 2–1 insertion represents a steric hindrance to further chain growth, often leads to a β-hydride elimination or via isomerization to a 1–3 insertion (135,166). Ethene as a comonomer also activates catalyst sites blocked by a 2–1 insertion (165).

Stereoselectivity in α-Olefin Insertion. Stereoregulation in the polymerization of α-olefins (30,31) 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 (164,167). The polymerization of propene to an isotactic polymer remains a unique example of stereoselectivity in organic, non-enzymatic reactions (164). How the stereochemical control is carried out will be outlined with the help of Figure 14. 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 (see Fig. 13). Before insertion, the propene molecule forms a weak π-complex in the 1–2 direction with the transition metal center (see Fig. 12). This coordination can be done in two prochiral positions (Figure 14**a** and **b**). If one of these is energetically favored, then the polymerization will be stereoselective. The spatial arrangement of the bridged metallocene is such that position **a** (Figure 14) 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 positions with each other. For the isotactic polymerization such a chain migration is no prerequisite because even without it, the meso stereosequences, ie, isospecific behavior would result, but the exchange of positions follows from the insertion model presented in Figure 12 and strong evidence is especially provided by the syndiotactic polymerization behavior of the C_s-symmetrical metallocene catalysts (see Fig. 13) (168).

When the insertion occasionally takes place via the other prochiral position (**b** in Fig. 14) a racemic diad is obtained (**b**→**d**). If the catalyst shows high isospecific behavior and in case of an enantiomorphic site control this stereoerror is immediately corrected (giving a second racemic diad (**d**→**e**) and remains isolated. The resulting *mrrm* (*mmrr*) pentad sequences (see the section Control of Polypropene Microstructure) are then typical for enantiomorphic site control.

Figure 15 illustrates the syndiotactic propagation with a C_s-symmetric cyclopentadienyl–fluorenyl catalyst (see also Fig. 17i and the section C_s-Symmetric Bridged Metallocenes). Strong evidence for the chain migration with every insertion step (cf. Figs. 12 and 14) is provided by the syndiotactic polymerization behavior of the C_s-symmetrical catalysts. For the syndiotactic polymerization an exchange of chain and monomer positions (chain migratory insertion) is a prerequisite because without it, meso stereosequences, ie, an isoselective behavior would be expected (168). Blockage of the chain migratory insertion by the *tert*-butyl group in $Me_2C(C_5H_3{-}3t\text{-}Bu)(Flu')ZrCl_2$ led indeed to an isotactic microstructure (78% *mmmm* pentad) through a so-called "stationary

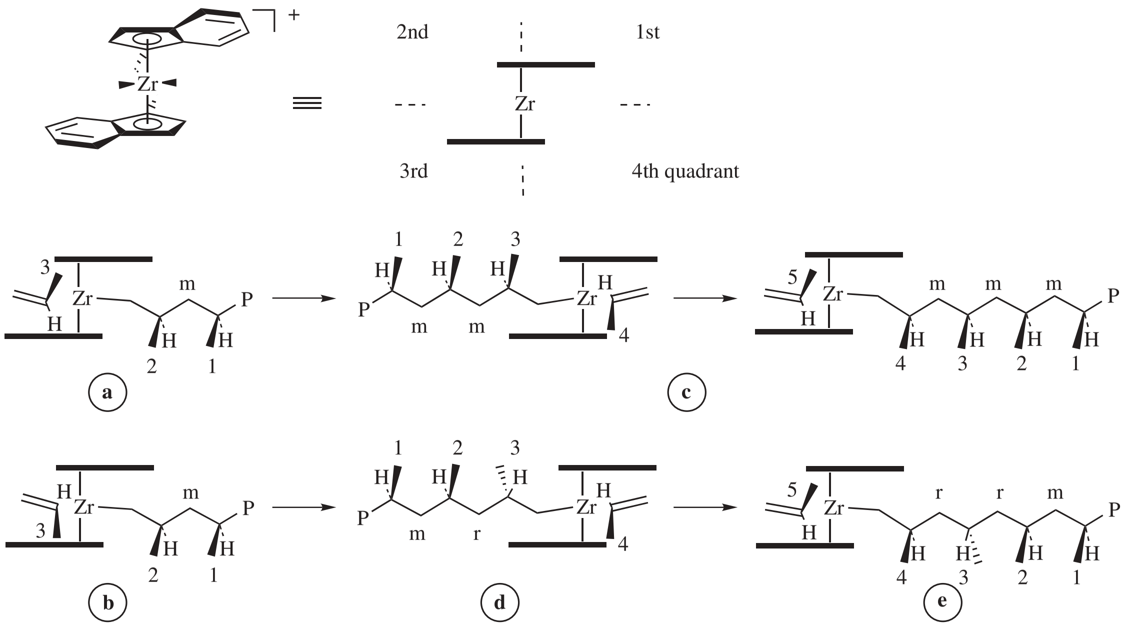


Fig. 14. Schematic model of the active complex for one enantiomeric form of the C_2-symmetrical metallocene C_2H_4 (Ind') $ZrCl_2$ with the two possible prochiral positions (**a** and **b**) of the 1,2-coordinated propene molecule. Position **a** is the energetically favored one. The steric demand of 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*) stereosequence results (**c**). The disfavored insertion from position **b** then leads to a stereoerror, a racemic stereosequence (**d**). Because of the enantiomorphic 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 (cf. Fig. 12). In reality, the chain flip between "left and right" involves only a small relative motion between chain end and metallocene.

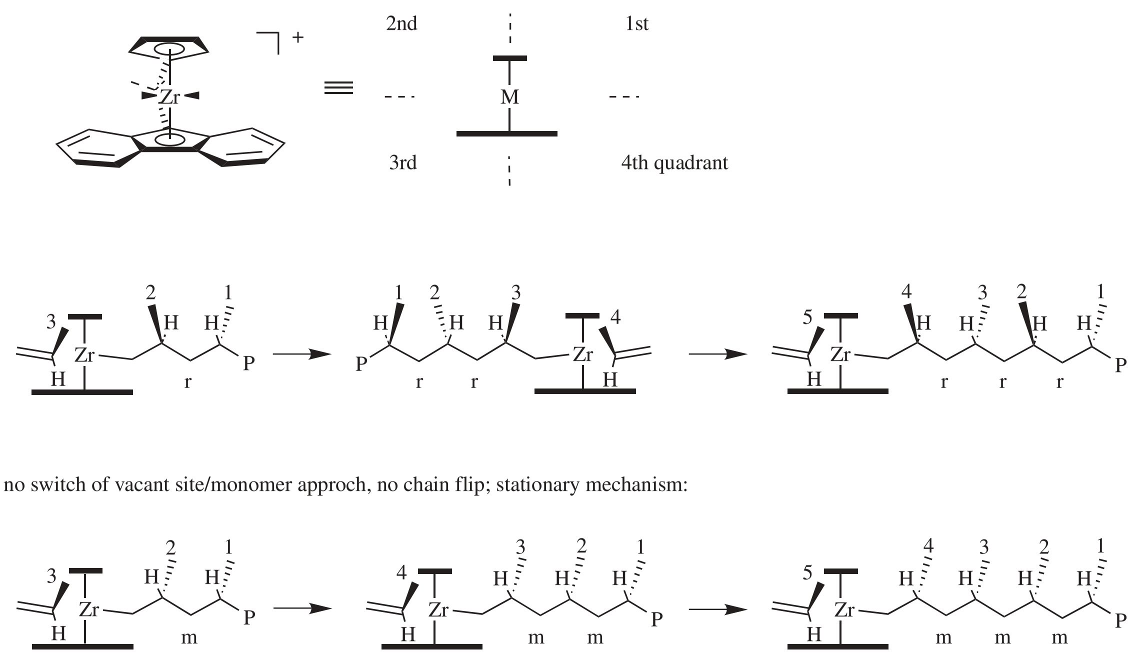


Fig. 15. Principle of syndiotactic propagation with a C_s-symmetric metallocene catalyst [here $Me_2C(C_5H_4)(Flu')ZrCl_2/MAO$] (170,171). The olefin approaches from alternating sides (as already illustrated for the isotactic insertion, see Fig. 14), but the steric demand of the fluorenyl ligand forces the growing chain and the propene methyl group into an orientation in the first and second quadrant, respectively, so that racemic (*r*) stereosequences result. In reality the chain flip between "left and right" involves only a small relative motion between chain end and metallocene. Without the switch in vacant site/monomer approach, ie, in a "chain stationary insertion mechanism", an isotactic microstructure would result as was found for $Me_2C(C_5H_3{-}3{-}t\text{-}Bu)(Flu')ZrCl_2$ (78% *mmmm* pentad) (169).

mechanism" (169) (see the section Chiral, C_1-Symmetric (Asymmetric) Bridged Metallocenes and C_s-Symmetric Bridged Metallocenes). The site or quadrant around the *tert*-butyl group is prohibited to the sterically demanding polymer chain and vacant for monomer coordination only. The opposite site/quadrant is the only position where the polymer chain can grow. Even without the switch in vacant site/monomer approach, the *tert*-butyl group and fluorenyl ligand provide for a preference for only one of the propene prochiral faces so that an isotactic polypropene results (see Fig. 15 lower part) (169).

5.2. Chain Transfer Processes. The two main chain-transfer processes observed with metallocene catalysts are

- Chain transfer by β-H elimination to the metal center (172). This leads to an olefinic end group and a metal hydrido species.
- Chain transfer to the aluminum cocatalyst. This gives a saturated end group after hydrolytic workup. Additional important chain transfer processes are
- β-H transfer to monomer.
- Hydrogenolysis by added H_2 (31,67,173).

For propene, a β-methyl elimination is possible as a chain-transfer process in the special cases of decamethylmetallocene catalyst system $(C_5Me_5)_2MCl_2$/MAO ($M = Zr$, Hf) (5,92,174) or $[(C_5Me_5)_2ZrMe]^+[MeB(C_6F_5)_3]^-$ (137). The chain transfer processes are schematically depicted in Figure 16. Kinetic studies, polymer molar mass dependence on monomer concentration (175) or an end-group analysis by ^{1}H and ^{13}C nmr spectroscopy in low molar mass polyolefins (174) can be used to determine the type of chain transfer process.

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 (29,176). 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 (see the section Chain-Transfer Process, Fig. 16) (177,178).

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 (179), catalyst formulation with support materials (45), 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 stereoselectivity of the metallocene strongly affects the activity (180–182). One has to be aware that 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,

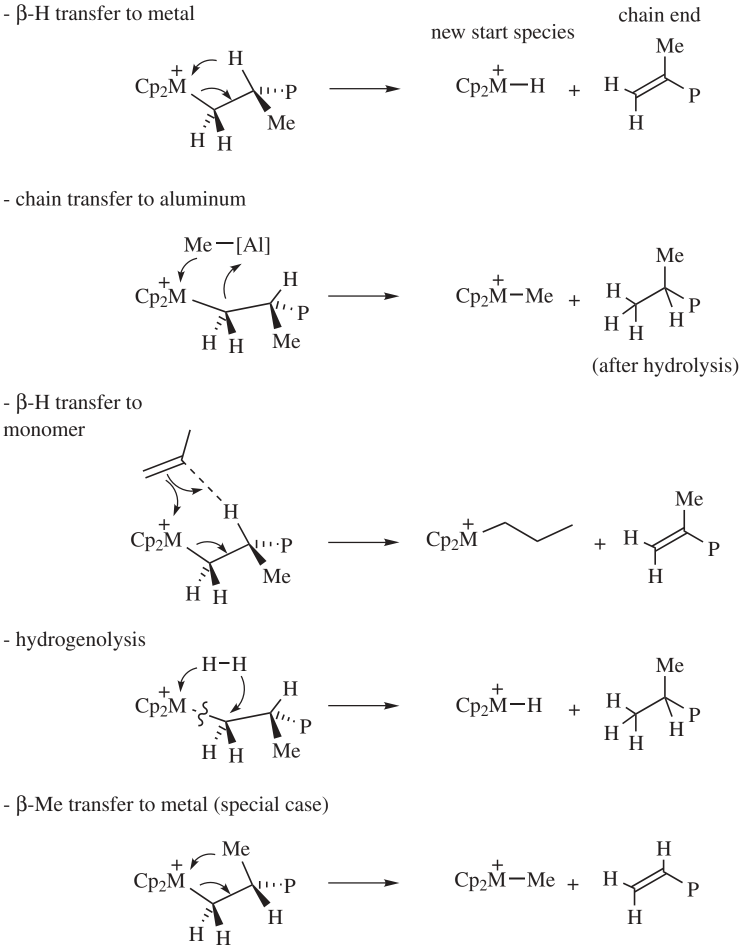


Fig. 16. Chain transfer processes with metallocene catalysts.

which represents a transfer to the heterogeneous phase (44). This leads to a diffusion-controlled reaction (6,84,129,133,183) and can no longer be compared in other terms.

Activity data for related metallocene complexes is often taken from the sources of other workers. Such a comparison should be judged with care because of the unavoidingly different polymerization conditions. The large number of obvious and less obvious parameters often renders such comparisons rather dubious. Obvious activity parameters are, eg, temperature, Al/Zr concentration, pressure, and solvent; less obvious are zirconocene concentration, quality of MAO (degree of oligomerization, age, TMA content) (108), monomer purity, pre- activation times between the zirconocene and MAO, reactor preparation, stirrer frequency, etc. The custom to collect activity data from the literature for comparison may be the source of many of the conflicting ideas (41) in metallocene catalysis.

7. Propene Homopolymerization

Generally, five different catalyst symmetries may be distinguished for the stereoselective propene polymerization (29–31):

(*1*) Achiral, C_{2v}-symmetric metallocenes like $(C_5H_{5-n}R_n)_2ZrCl_2$ (Fig. 17**a**)

(*2*) Chiral, C_2-symmetric (dissymmetric) bridged and unbridged metallocenes like $Me_2Si(2\text{-}Me{-}Ind'')_2ZrCl_2$ (Fig. 17**b**), $(1\text{-neomenthyl-}Ind')_2ZrCl_2$ (Fig. 17**c**), $(1\text{-}Me{-}Flu')_2ZrCl_2$ (Fig. 17**d**)

(*3*) Chiral, C_1-symmetric (asymmetric) bridged metallocenes like $Me_2C(C_5H_4)(Ind')ZrCl_2$ (Fig. 17**e**), $Me_2C(C_5H_3\text{-}3{-}t\text{-}Bu)(3\text{-}t\text{-}Bu{-}Ind'')ZrCl_2$ (Fig. 17**f**), $Me_2Si(C_5Me_4)(C_5H_3{-}3\text{-neomenthyl})ZrCl_2$ (Fig. 17**g**)

(*4*) Oscillating unbridged metallocenes like $(1\text{-neomenthyl} - Ind')_2ZrCl_2$ (Fig. 17**c**), $(1\text{-}Ph{-}Ind')_2ZrCl_2$ (Fig. 17**h**)

(*5*) C_s-symmetric bridged metallocenes like $Me_2C(C_5H_4)(Flu')ZrCl_2$ (Fig. 17**i**)

In addition to the experimental results described in the following, a variety of theoretical modeling studies are available (31,158). Such studies provide a valuable interplay between experiment and theory to substantiate or to adjust the initial hypotheses on the stereocontrol in the α-olefin polymerization with the various stereoselective catalysts (184,185). Modeling calculations have been carried out by, eg, ab initio molecular orbital (MO) and molecular mechanics (MM) methods on the selectivity control in propene polymerization with bridged metallocenes (186). An MM study is available on the back-skip of the growing chain at model complexes for various ethanediyl-bridged metallocenes (187). A density-functional theoretical (DFT) study investigated the influence of rotation between agostic structures on ethene interaction with a zirconocene polymerization site (188). A force-field (MM) study dealt with π-stacking as a control element in the oscillating $(2\text{-}PhInd')_2ZrCl_2$ catalysts (189). Additional theoretical studies may be mentioned below.

7.1. Achiral, C_{2v}-Symmetric Unbridged Metallocenes. Such metallocenes mostly give atactic and low molar mass polypropene at conventional polymerization temperatures (>50°C). This does not change even with bulky alkyl groups attached to the unbridged cyclopentadienyl or indenyl ligands in Cp_2ZrCl_2 to hinder the ring rotation (see the sections Chiral, C_1-Symmetric (Asymmetric) Bridged Metallocenes and Olefin Oligomerization) (5,92,182,190) unless rotation is sufficiently hampered to only an oscillatory movement about the metal-ring bonds (see the section Oscillating Unbridged Catalysts). Atactic polypropene almost always has a low molar mass and is an oily or waxy material (see the section Olefin Oligomerization). At low enough temperatures, eg, −45°C for $(C_5H_5)_2TiPh_2$ (92), achiral catalysts are, however, capable of polymerizing propene with chain-end stereocontrol.

7.2. Chiral, C_2-Symmetric Bridged Metallocenes. These metallocene–MAO catalysts afford isotactic polypropene. The chiral, C_2-symmetric metallocenes are typically based on the bis(indenyl)ligand with the two indenyl rings connected by a bridge (see Fig. 9, Figs. 17**b** and 19). However, chiral, C_2-symmetric *un*bridged metallocenes and chiral C_1-symmetric (asymmetric) metallocenes including

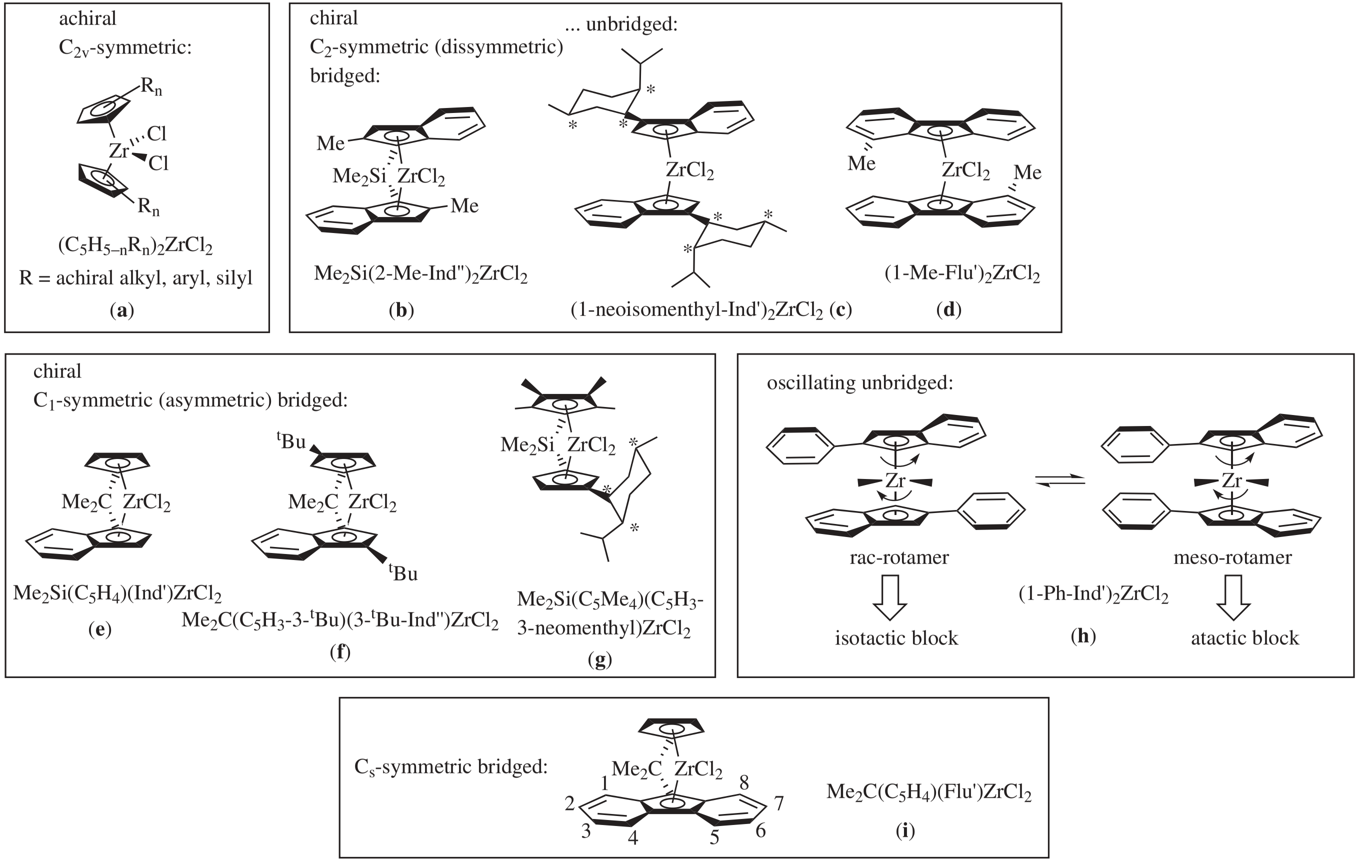


Fig. 17. Examples for the different metallocene symmetries relevant to stereoselective α-olefin polymerization. See text for further comments on the sketched metallocenes.

modifications of C_s-symmetric metallocenes can also yield isotactic polypropene (Fig. 7, see the sections Chiral C_2-Symmetric *Un*bridged Metallocenes, Chiral C_1-Symmetric (Asymmetric) Bridged Metallocenes, and C_s-Symmetric Bridged Metallocenes, respectively).

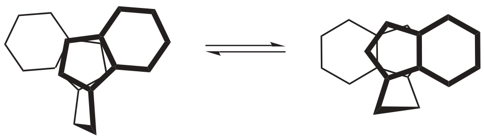
Since propene polymerization is usually carried out only in a stereoselective and not an enantioselective manner, it suffices to use the racemic (*rac*) mixture of the precatalyst. Only the achiral *meso* form has to be excluded (see Fig. 9). The enantiomers differ only in that they form polypropene chains of different (left or right) helical handedness (191). It can usually be assumed that the racemic mixture of chiral C_2-symmetric catalysts is employed in α-olefin polymerization. The prefix *rac*- may be used to indicate this fact, eg, *rac*-$C_2H_4(Ind')_2ZrCl_2$, but is omitted here for brevity.

The bridge between the rings can be modified to a large degree (192), eg, introducing additional stereocenters in the ethanediyl (193) or Me_2Si bridge (192) or by varying the bridge atom from Si to Ge (194,195) to Sn (196).

Still, for a long time it was a serious drawback that even chiral *ansa*-zirconocene–MAO catalysts produced only low molar mass oligomers at conventional polymerization temperatures >60°C, where the activity was high (89,98,197). The reason for obtaining oligomeric products is due to a larger increase of the rate of chain transfer (mainly by β-hydrogen elimination) versus the rate of chain propagation with the increase in temperature.

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) (Fig. 17**b**) gave polymers in higher yield and higher stereoselectivity (see Fig. 7) (198). The same was already found earlier for *ansa*-bis(cyclopentadienyl) systems (199,200). The remarkable effect of the α-methyl substituents may be traced to the suppression of 2-1- or tail-to-tail (mis)insertions (see Fig. 13). 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-irregularites are suppressed close to or below the detection limit (200). On the other hand, the methyl group is turned away from catalytically relevant spatial opening, 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 (198).

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 (201). To a certain degree that depends on their substitution pattern, *ansa*-metallocene complexes are fairly easily deformable. The bridged ligand framework can rotate up to ±20° about the metal-C_5-ring-centroid axes between two shallow energy minima leading to off-(C_2-)axially distorted conformers. Figure 18 sketches these two conformations for which an energy difference



δ-(R,R) conformation
Π (indenyl-forward)

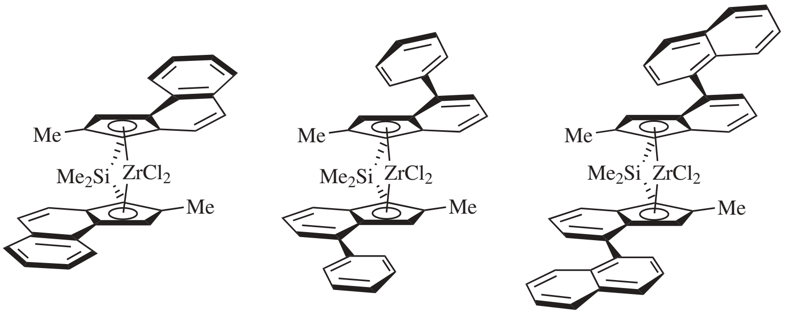
λ-(R,R) conformation
Y(indenyl-backward)

Fig. 18. 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 (202).

of 0.95 kcal/mol was deduced from temperature variable nmr, with the Y (indenyl-backward) conformation suggested to be the "higher" energy conformer (202). An unrestricted fluctuation in solution between these two conformations has implications for structure-function correlations in olefin polymerization (201).

The above findings may have led to the synthesis of doubly bridged zirconocenes $(Me_2Si)_2Cp''_2MCl_2$ (Cp″ = disubstituted cyclopentadienyl, M = Ti, Zr), where stereoselectivity ranges from atactic to syndiotactic in propene polymerization (203–206).

Eventually the problem of oligomeric molar mass of polypropene at conventional reaction temperatures of 50°C and higher seemed to have been overcome with the introduction of *ansa*-zirconocene complexes carrying additional aromatic substituents on the six-membered indenyl moiety, either anellated as in Me_2Si(2-Me-benz[*e*]indenyl)$_2ZrCl_2$ (Fig. 19**a**) (207) or sigma-bonded in appropriate positions as in Me_2Si(2-Me-4-phenylindenyl)$_2ZrCl_2$ (Fig. 19**b**) or in Me_2Si{2-Me-4-(1-naphthyl)indenyl}$_2ZrCl_2$ (Fig. 19**c**) (208). The complexes in Figure 19**a**–**c** are examples of the so-called "advanced metallocenes" that give activities, stereoselectivities, and polypropene molar masses much higher than those of any previously described metallocene system (208,209). The anellated benz[*e*]indenyl complex in Figure 19**a** leads to a considerable gain in activity compared to



Me_2Si(2-Me-benz[e]indenyl)$_2ZrCl_2$
(**a**)

Me_2Si(2-Me-4-phenylindenyl)$_2ZrCl_2$
(**b**)

Me_2Si{2-Me-4-(1-naphthyl)indenyl}$_2ZrCl_2$
(**c**)

Fig. 19. Examples for so-called "advanced metallocenes" (precatalysts), yielding polypropene of high molar mass even at temperatures >50°C.

the standard *ansa*-bis(indenyl) system because the former catalyst is deactivated at an unusually low rate with an about three times longer half-life. Again, a direct comparison of the complex in Figure 19**b** with and without α-methyl substituents revealed the molar mass enhancing properties (by a factor of 4) of the methyl groups (207,210).

7.3. Chiral, C_2-Symmetric Unbridged Metallocenes. Metallocenes of this type could, eg, be prepared with the help of chiral auxiliaries, such as cholestanyl (211), neoisopinocamphyl (212), neomenthyl, and neoisomenthyl (213) that were attached to unbridged indenyl and tetrahydroindenyl ligands (Fig. 17**c**). Only at low temperature did the resulting zirconocene complexes (activated by MAO) produce high molecular weight polypropene with enantiomorphic-site control. 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. oscillating catalyts the section Oscillating Unbridged Catalysts). 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 (213).

With the appropriate ligands unbridged, C_2-symmetric metallocene catalysts could, however, polymerize propene to crystalline isotactic polypropene even at conventional polymerization temperatures. Bis(1-methylfluorenyl)zirconium dichloride (Fig. 17**d**) after activation with MAO gave at 60°C a polymer which was 83% isotactic (*mmmm* pentad, Fig. 7). The activity was 5300 g PP/(g Zr · h) in liquid propene. An analysis of the polymer microstructure showed *mrrm*/*mmrr* sequences that are consistent with an enantiomorphic-site stereochemical control mechanism (see the section Control of Polypropene Microstructure) (214). It is noteworthy that a bridged bis(fluorenyl)zirconium complex gave predominantly atactic polypropene, albeit of high molecular mass (215). When a phenyl group was placed on the C_5 ring (the 9-position) in Figure 17**d** no propene and only low ethene polymerization activity was observed due to blocking of the insertion path by the bulky 9-substituent (216).

7.4. Chiral, C_1-Symmetric (Asymmetric) Bridged Metallocenes. Metallocene complexes with the *ansa*-cyclopentadienyl-indenyl backbone (Fig. 17**e**) produce homopolypropenes with excellent thermoplastic elastomeric properties attributable to isotactic-atactic stereoblock or hemiisotactic microstructures (see Fig. 7) (217). 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 Me_2C (C_5H_4) $(Ind')ZrCl_2$ complex (Fig. 17**e**) experimental and modeling studies were able to describe such polymer structures (185). 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 (218). With the appropriate bulky substitution, such as in $Me_2C(C_5H_3\text{-}3\text{-}t\text{-}Bu)(3\text{-}t\text{-}Bu\text{-}Ind'')ZrCl_2$ shown in Figure 17**f**, the polymerization of propene was found to afford highly isotactic polymers (>0.99 *mmmm*, see

Fig. 7) of medium to high molecular weight (219). From a dimethylsilyl-bridged bis(cyclopentadienyl) complex, where one of the cyclopentadienyl rings carries a neomenthyl group as a chiral auxiliary (Fig. 17**g**), the products were of low molar mass and only at low temperature (0 to −45°C) was the isotacticity (by *mmmm* pentad) >90% (220). In the absence of the bridge, usually a fast ring rotation results yielding essentially C_{2v}-symmetric complexes with little stereocontrol (see the section Achiral, C_{2v}-Symmetric Unbridged Metallocenes) unless rotation is sufficiently hindered to only an oscillatory movement about the metal-ring bonds (see the section Oscillating Unbridged Catalysts).

Chiral C_1-symmetric catalysts are also derived from C_s-symmetric $Me_2C(C_5H_4)(Flu')ZrCl_2$ metallocenes, eg, through substitution on the Cp ring. A *tert*-butyl ligand on the cyclopentadienyl ring (in the β-position relative to the bridge) gives the isotactic-selective (78% *mmmm* pentad) C_1-symmetric metallocene complex $Me_2C(C_5H_3\text{-}3\text{-}t\text{-}Bu)(Flu')ZrCl_2$ (section Stereoselectivity in α-Olefin Insertion, Fig. 15) (169). A methyl substitutent on the Cp ring gives the complex $Me_2C(C_5H_3\text{-}3\text{-}Me)(Flu')ZrCl_2$ that polymerizes propene in a distereoselective manner to give isotactic-syndiotactic stereoblock PP (221) (see the section C_s-Symmetric Bridged Metallocenes for an explanation of the polymerization mechanism). The ethanediyl bridged 2-Me-benz[*e*]indenyl containing C_1 metallocene C_2H_4(2-Me-benz[*e*]indenyl)(Flu′)$ZrCl_2$ yields isotactic–atactic stereoblock polypropene (222) (see also Fig. 7).

7.5. Oscillating Unbridged Catalysts. In unbridged metallocenes, ring rotation may be sufficiently hindered to only an oscillatory movement about the metal-ring bonds. The concept is based on unbridged bis(indenyl) and -(tetrahydroindenyl) ligands with, eg, bulkyl chiral groups such as cholestanyl (211), neoisopinocamphyl (212) neomenthyl, and neoisomenthyl (Fig. 17**c**) (213), so that torsional isomers become possible. The concept is illustrated with the phenyl substituted indenyl catalyst derived from the compound $(1\text{-}Ph\text{-}Ind')_2ZrCl_2$ (Fig. 17**h**) (223). 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. Both rotamers exercise a different stereocontrol in propene insertion corresponding to an isotactic–atactic stereoblock polymerization (see Fig. 7). 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 (223,224).

7.6. C_s-Symmetric Bridged Metallocenes. C_s-Symmetric catalysts, such as $Me_2C(C_5H_4)(Flu')ZrCl_2$/MAO, where the metal carries a bridged cyclopentadienyl and fluorenyl ligand (Fig. 17**i**) typically yield syndiospecific polypropene with some isotactic triads (*mm*) as defects (see Fig. 7). The first report on this remarkable new syndiospecific polymerization with hafnium and zirconium metallocenes appeared in 1988 (170). Up to this time syndiotactic PP could mainly be obtained in vanadium-catalyzed polymerizations below −50°C (164,225) but not with classical Ziegler-Natta catalysts. [For a morphological study on syndiotactic PP prepared by *ansa*-metallocenes, see (226).]

Seemingly small variations in the ligand structure of C_s-symmetric catalyst can have a significant effect on the stereoselectivity (171): The closely related silylene bridged derivative $Me_2Si(C_5H_4)(Flu')ZrCl_2$ when activated with

MAO catalyzed the propene polymerization nonstereoselectively without any syndiotactic tendency (195,227). A *tert*-butyl ligand on the Cp ring gives the isotactic-selective metallocene complex $Me_2C(C_5H_3\text{-}3\text{-}t\text{-}Bu)(Flu')ZrCl_2$ (78% *mmmm* pentad) (169) (the section Chiral, C_1-Symmetric (Asymmetric) Bridged Metallocenes, see also Fig. 7). The microstructure is explained by a blockage of the migratory insertion (chain flip) by the bulky β-*tert*-butyl group (cf. the section Stereoselectivity in α-Olefin Insertion, Fig. 15). The site or quadrant around the *tert*-butyl group is prohibited to the sterically demanding polymer chain and vacant for monomer coordination only. The opposite site/quadrant is the only position where the polymer chain can grow. Hence, monomer insertion proceeds by a so-called "stationary mechanism" (chain stationary insertion). Even without the switch in vacant site/monomer approach, the *tert*-butyl group and fluorenyl ligand provide for a preference for only one of the propene prochiral faces so that an isotactic polypropene results (see Fig. 15 lower part) (169).

An additional methyl substituent on the cyclopentadienyl ring in $Me_2Si(C_5H_3\text{-}3\text{-}Me)(Flu')ZrCl_2$ (in the β-position relative to the bridge, Fig. 17**i**) gives a complex that polymerizes propene in a distereoselective manner to give isotactic–syndiotactic stereoblock PP (221). Here the microstructure is explained by a periodical alternation between a multiple of chain migratory insertions (to give the syndiotactic blocks) and a few chain stationary insertion steps (to give the isotactic blocks). The size of the β-methyl substituent (when compared to the β-*tert*-butyl group above) still permits the periodical migration of the chain to the more crowded position. A (concerted) haptacity change of the $C_5H_3{-}Zr$ bonding is suggested to help in the site-switching (221).

Substituents on the sterically little active positions 2 and 7 of the fluorenyl moiety (cf. numbering in Fig. 17**i**) do not affect the syndioselectivity of the catalyst but have large effects on the activity (228). With no bridge present as in $(C_5H_5)(Flu)ZrCl_2$, or ligand substituted derivatives thereof, only atactic polypropene is formed. This is 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 (229). The influence of substituents on the bridge-head atom in $RR'C(C_5H_4)(Flu')ZrCl_2$/MAO on the propene polymerization activity has been found to increase in the order MeMe $\approx$ MePh $\approx$ $(CH_2)_4$ $<$ HH $<$ HPh $<$ $(CH_2)_5$ $<$ PhPh. The PP molar mass is much higher (by a factor of 5 or 6) for $RR' =$ MePh or PhPh (230).

8. Homopolymerization of Other α-Olefins

In catalytic alkene polymerization with metallocene catalysts, the molar mass of polyalkenes and the reaction rates decrease in the order ethene > propene > 1-butene > 1-pentene > 1 hexene. Examples of other olefins polymerized with metallocene catalysts include 1-butene (166,231) [with C_2H_4 $(Ind'H_4)_2ZrCl_2$/MAO (98) or $Me_2Si(Ind'H_4)_2ZrCl_2$/MAO (232), 1-pentene (with $Me_2C(C_5H_4)(Flu')ZrCl_2$/MAO (233)], 1-hexene (234) [with $C_2H_4(Ind')_2ZrCl_2$ (235)], and 3-methyl-1-butene (236).

9. Olefin Oligomerization

Initially, the finding of low molar mass products from propene polymerization with zirconocene catalysts was generally regarded as unfortunate (89,92,98, 197,237,238). Now, it is recognized that metallocene catalysts may be used effectively for the directed oligomerization of α-olefins (5,182,239–243) to give oligomers with 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 (239,241,244,245).

Olefin oligomerization is also used to study mechanistic aspects of metallocene catalysis because of the homogenity of the system (no heterogenization through polymer precipitation) and because the oligomeric products are easier to analyze than high molar mass polymers (92,167,174,246,247).

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 (see Fig. 6).

Examples of copolymerization studies with ethene are summarized in Table 1.

Copolymerization of ethene with 1,3-butadiene or 5-vinyl-2-norbornene yields polyethenes with pendant olefinic groups that can be further converted to give functional olefins (90,262). The complex $C_2H_4(Ind')_2ZrCl_2$/MAO is an excellent catalyst for the ethene (E), propene (P), and ethylidine norbornene (268) or octa-1,6-dienes (269) (D, as diene) terpolymerization with as much as 20% D uniformly incorporated into the EPDM–terpolymer. The EPDM terpolymers with the same components could also be prepared by means of $(C_5H_5)_2ZrMe_2$/MAO (270).

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 that were blocked by a preceding 2-1 insertion (see the section Regiospecificity in α-Olefin Insertion), which normally leads to β-hydride elimination and chain growth termination (165).

A propene–1-octene copolymerization with the syndioselective catalyst $Me_2C(C_5H_4)(Flu')ZrCl_2$/MAO (see Fig. 17**i**) showed again random incorporation of large amounts of 1-octene. The polymer parameters were studied as a function of octene content (271). 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 isoselective catalyst $C_2H_4(Ind')_2HfCl_2$/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 (272).

For the copolymerization of ethene and propene with polar, functional monomers see the Section Polymerization of Polar Monomers.

Table 1. **Examples of Ethene Copolymerization Studies with Metallocene Catalysts**

Monomer/comonomer	Metallocene catalyst[a]	References
ethene/propene	$(C_5H_5)_2ZrCl_2$/MAO	248,249
	$C_2H_4(Ind')_2ZrCl_2$, $C_2H_4(Ind'H_4)_2ZrCl_2$/MAO compared to unbridged metallocene catalysts	250
ethene/isobutene	$Me_2Si(C_5Me_4)$(Ncyclodecyl)$TiMe_2$/MAO or borate	251
ethene/1-hexene	$C_2H_4(Ind')_2ZrCl_2$, $C_2H_4(Ind'H_4)_2ZrCl_2$/MAO compared to unbridged metallocene catalysts	252
	$(C_5H_5)_2ZrCl_2$, $Me_2Si(C_5H_4)_2ZrCl_2$, $C_2H_4(Ind')_2ZrCl_2$, $(Ind)_2ZrCl_2$/MAO	253
	$C_2H_4(Ind')_2ZrCl_2$, $(C_5H_5)_2ZrCl_2$/MAO	254
	$(C_5H_5)_2ZrCl_2$/MAO	255
	$Me_2C(C_5H_4)(Flu')ZrCl_2$	256
ethene/1-octene	$(C_5H_5)_2ZrCl_2$, $Me_2Si(C_5H_4)_2ZrCl_2$, $C_2H_4(Ind')_2ZrCl_2$, $(Ind)_2ZrCl_2$/MAO	253
	$(C_5H_5)_2ZrCl_2$/MAO	257
	R_2Si(2-Me-benz[*e*]indenyl)(N-*t*-Bu)$TiCl_2$	258
ethene/1-dodecene	$Me_2C(C_5H_4)(Flu')ZrCl_2$, $Me_2Si(Ind')_2ZrCl_2$/MAO	259
ethene/1-tetradecene	$(C_5H_5)_2ZrCl_2$/MAO	257
ethene/1-octadecene	$Me_2C(C_5H_4)(Flu')ZrCl_2$, $Me_2Si(Ind')_2ZrCl_2$/MAO	256,259
	$(C_5H_5)_2ZrCl_2$, $(C_5H_5)_2HfCl_2$/MAO	257,260
ethene/1,3-butadiene	$(C_5H_5)_2ZrCl_2$/MAO	90
ethene/norbornene	$Me_2C(C_5H_4)(Ind')ZrCl_2$, $Me_2C(C_5H_3Me)(Ind')ZrCl_2$, $Me_2C(C_5H_3$-3-*t*-Bu)(Ind′)$ZrCl_2$/MAO	261
ethene/5-vinyl-2-norbornene	$(C_5H_5)_2ZrCl_2$/MAO	262
ethene/2-allylnorbornane	$(C_5H_5)_2ZrCl_2$/MAO	263
ethene/4-vinylcyclohexene	$Ph_2C(C_5H_4)(Flu')ZrCl_2$/MAO	264
ethene/4-methyl-1-pentene	$C_2H_4(Ind')_2ZrCl_2$, $(C_5H_5)_2ZrCl_2$/MAO	265
ethene/styrene	$C_2H_4(Ind')_2ZrCl_2$/MAO	266
	$Me(Ph)C(C_5H_4)(Flu')ZrCl_2$/MAO/TMAy2	267
	$Me_2Si(C_5H_4)(NR)TiCl_2$	25,26

[a] Ind′ = indenyl connected to one other ligand or substituent, C_9H_6. Ind = free indenyl, C_9H_7. Flu = free fluorenyl, $C_{13}H_9$. *t*-Bu = *tert*-butyl. Flu′ = fluorenyl connected to another ligand or substituent, $C_{13}H_8$. TMA = trimethylaluminum, Me_3Al. Me = methyl, CH_3. Ph = phenyl, C_6H_5.

11. Polymerization and Copolymerization of Cyclic Olefins

The metallocene–MAO catalyst systems allow polymerization of cyclic olefins with no ring opening taking place (273,274). With chiral metallocenes, cycloolefins like cyclobutene, cyclopentene, and norbornene can be polymerized to give isotactic polymers. For polycyclopentene, contrary to the initial formulation as a 1-2 insertion product (275), it was later proven that incorporation proceeded in a cis- and trans-1-3 manner (Fig. 20) to give poly(1,3-cyclopentene) (276). From $C_2H_4(Ind')_2ZrCl_2$ and cyclopentene, isotactic polycyclopentene is obtained that is insoluble in aromatic or aliphatic hydrocarbons and highly crystalline with a melting point above the decomposition temperature (277).

In general, the polycycloalkenes show extremely high melting points that lie above their decomposition temperatures (in air). Under vacuum the melting

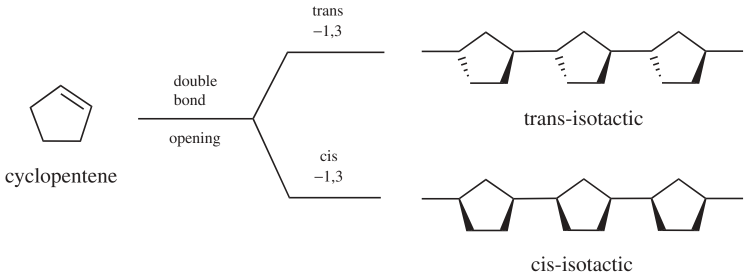


Fig. 20. Polycyclopentene from metallocene catalysis—cycloolefin polymerization without ring opening.

points were found (by DSC) to be 485°C for polycyclobutene, 395°C for polycyclopentene, and >600°C for polynorbornene (274,275). Such high melting points make the homopolymers difficult to process. To lower the melting points, the cycloolefin can be copolymerized with ethene or propene. Now, it was possible with metallocene catalysts to solve a decade old problem, viz, the technical synthesis of cycloolefin-copolymers (COCs) (273). 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 $(C_5H_5)_2ZrCl_2$ (275).

The norbornene–ethene copolymer features a high glass transition temperature, excellent transparency, thermal stability, and chemical resistance. It is suggested that these materials could be used for optical disks and fibers. With $C_2H_4(Ind'H_4)ZrCl_2$/MAO, ethene is inserted only 1.5–3.2 times faster than norbornene and copolymers containing >50 mol% of norbornene units can be made; if the norbornene concentration is >60 mol%, a glass transition point of ~120°C can be reached (278). On the basis of a norbornene–ethene copolymer, the companies Hoechst (now Ticona) and Mitsui Chemicals 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, magneto-optic storage disks or packaging materials (279).

12. Polymerization of Polar Monomers

The use of Group 4 (IVB) metallocenes as initiating systems for the synthesis of polar or functional monomers has also been reported (280). Although, here in some cases it is more reasonable to assume not a Ziegler-Natta type insertion but a cationic polymerization reaction (281,282). For 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 (283). On the other hand, $(C_5H_5)_2ZrMe_2$, $C_2H_4(Ind')_2ZrCl_2/[Ph_3C][B(C_6F_5)_4]$, $C_2H_4(Ind'H_4)_2ZrCl_2/[Ph_3C][B(C_6F_5)_4]$, and $Me_2Si(Ind')_2ZrCl_2/[Ph_3C][B(C_6F_5)_4]$ were found to be inactive toward the polymerization of MMA without the addition of a Lewis acid such as dialkylzinc and alkylaluminum compounds (284). The $Me_2C(C_5H_4)(Flu')ZrCl_2$ failed to initiate the polymerization of MMA even under these conditions (284c). The polymerization of polar monomers such as alkyl acrylates can also be initiated by Group 3 (IIIB) and lanthanoide metallocenes, eg, $(C_5Me_5)_2LnMe(thf)$ (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 distributions (22).

Typical C_2-symmetrical *ansa*-zirconocene catalysts, such as $C_2H_4(Ind')_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ together with [bis(2,6-di-*tert*-butyl-4-methylphenoxy)methyl]aluminum as activator were reported for the synthesis of predominantly isotactic poly(*tert*-butylacrylate) and highly isotactic poly(methyl methacrylate) (285). Cationic Group 4 (IVB) metallocene catalysts derived from the reaction of $(C_5Me_5)_2ZrMe_2$ or $C_2H_4(Ind'H_4)_2ZrMe_2$ with $B(C_6F_5)_3$ or [*N*,*N*-dimethylanilinium]$[B(C_6F_5)_4]$ are active catalysts for the homo- or copolymerization of α-olefins containing silyl-protected alcohols and tertiary amines (286,287).

Copolymers of propene and a polar sterically hindered phenolic monomer were obtained with $Me_2Si(Ind'H_4)_2ZrCl_2$/MAO, containing from 1.3 to 5.5 wt.% of comonomer. The addition of the polar 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 (288). Ethene could also be copolymerized with 10-undecene-1-ol using $(C_5H_4\text{-}n\text{-}Bu)_2ZrCl_2$/MAO; the bimodal molar mass distribution curve of the polymers indicated, however, the presence of two or more active sites in the catalyst (289). Zirconocene–MAO catalysts could to some extent also polymerize ethene and propene with 1-chloro-10-undecene (290), 1-$(Me_3Si)_2$amino-10-undecene (291), silsesquioxane-functionalized decene (292), an *ortho*-heptenyl-phenol derivative (293), and borane-functionalized α-olefins (294).

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