

Effect of the Nature of Metallocene Complexes of Group IV Metals on Their Performance in Catalytic Ethylene and Propylene Polymerization

Helmut G. Alt* and Alexander Köppl

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

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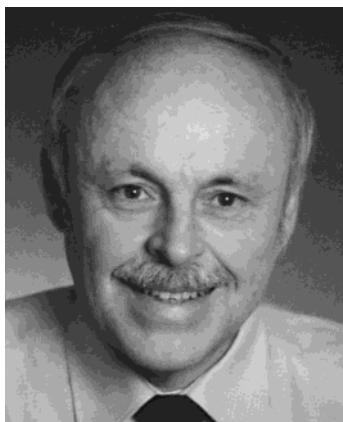
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I. Introduction

One of the biggest challenges for modern organometallic chemistry is its application in new technologies and new materials. For this purpose, in many cases already known types of complexes have been synthesized, modified, and applied for new catalytic processes or applications.

One of the hottest areas in this respect are metallocene complexes with group IV metals. In the past 10 years they initiated a renaissance in the field of catalytic olefin polymerization^{1–7} that was established in the 1950s with Ziegler–Natta and Phillips catalysts. A flood of reviews and books is illustrating the situation.^{8–14} Why are metallocene catalysts so attractive?

(1) The homogeneous nature of these catalysts provides active sites for every molecule in solution and explains their enormous activity. They can be a



Helmut G. Alt was born in 1944. He received his chemical education at the Technische Universität München. After his Ph.D. work with Max Herberhold, he spent nearly two years as a postdoctoral fellow with Marvin D. Rausch at the University of Massachusetts. He returned to Munich in 1975 for his Habilitationsarbeit and then moved to the newly founded University of Bayreuth in 1978 where he finished his Habilitation in 1980. In 1993 he received a call for a chairholder position in Chemnitz but preferred to stay in Bayreuth as an Extraordinary Professor of Chemistry. He has published more than 200 papers and is the inventor/coinventor of numerous patents. His main research interests are catalytic processes and especially olefin polymerization.



Alexander Köppl was born in Vilseck, Germany, in 1970. He received his chemical education and his Ph.D. degree at the University of Bayreuth. His dissertation in the research group of Professor H. G. Alt dealt with new support materials for the immobilization of cocatalytically active alumoxanes and their application in ethylene homopolymerization and ethylene/ α -olefin copolymerization. He is currently a chemist for BASF AG in Ludwigshafen, Germany.

100 times more active than conventional Ziegler–Natta or Phillips catalysts. The *ansa* bis(fluorenyl) complex $(C_{13}H_8-C_2H_4-C_{13}H_8)ZrCl_2$, for instance, produces 300 t of PE/g of Zr·h at 70 °C after activation with a cocatalyst.¹⁵

(2) Their potential to polymerize prochiral olefins, such as propylene, to give stereospecific polymers (isotactic,⁴ syndiotactic,¹⁶ hemitactic¹⁷ polypropylene). This variety opens the door to polyolefin elastomers.

(3) Their ability as so-called “single site” catalysts to produce polyolefins with narrow molecular weight distributions ($M_w/M_n \approx 2$).

(4) Their potential for producing polyolefins with regularly distributed short- and long-chain branches in the polymer chain. These parameters determine the properties of new materials for new applications (for instance mLLDPE) and thus generate new markets.

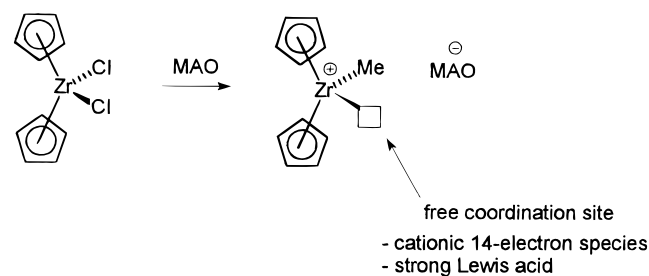
(5) The heterogenization of these catalysts provides different active sites than those in solution and can have an enormous effect on the catalyst activity and the properties of the produced polyolefins in terms of molecular weights, branching, and stereospecificity.

II. General Aspects of Metallocene Catalysts

II.1. Activation of the Catalyst Precursors

To understand the nearly unlimited versatility of metallocene complexes, it is necessary to take a closer look at the catalyst precursor and its activation process with the cocatalyst methylalumoxane (Scheme 1).

Scheme 1. Activation of the Metallocene Complex Cp_2ZrCl_2



In most cases the catalyst precursor is a metallocene dichloride complex consisting of two aromatic five-membered ring systems that can be tethered by a bridging unit (*ansa* metallocene complexes) or not. The two aromatic ligands at the metal can be of the same type, i.e., cyclopentadienyl, indenyl, or fluorenyl. The introduction of substituents at certain positions of the two aromatic ligands and/or the bridge modifies not only the steric and electronic conditions in the molecule but also the symmetry of such a metallocene dichloride complex. Another variable parameter is the metal: $M = Ti, Zr, Hf$.

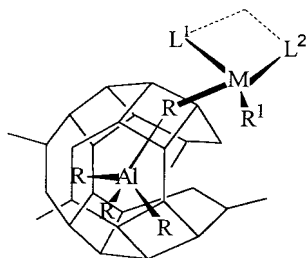
II.2. The Role of the Cocatalyst

A comprehensive contribution to this topic is provided by Chen and Marks in this issue. Therefore, only a small summary is given.

A metallocene catalyst precursor can be activated with organoalumoxanes, especially methylalumoxane, which provides maximum activity.^{18–24} The activation reaction is comprised of first the methylation of the central metal and second a carbanion abstraction to produce a metallocene monomethyl cation as the actual catalytic species.^{25–30} This theory is supported by the fact that strong Lewis acids, e.g. $B(C_6F_5)_3$, abstract a methyl anion from dimethylated complexes of the type Cp_2MMe_2 to form a cationic species Cp_2MMe^+ that is the actual catalyst for the polymerization of olefins.^{31–34} In contrast to MAO, borates, especially the perfluorinated tri- or tetra-aryl derivatives, can be applied stoichiometrically to give activities that can be compared with those obtained from MAO. The disadvantage of this class of cocatalysts is their high price and the incorporation of fluorine into the polymer, which can cause problems when polyolefins are thermally decomposed.

MAO is the reaction product of the partial hydrolysis of trimethylaluminum. It can be described as a mixture of linear and cyclic oligomers that coexist in a dynamic equilibrium.^{35–38} Barron characterized *tert*-butylalumoxane as a $[\text{tBuAlO}]_6$ cage with four-coordinated aluminum atoms.^{23,35,39,40} This may be an indication for a similar MAO structure as also suggested by Sinn.²⁴ However, the structure of MAO remains too complex, although it has been investigated by cryoscopic, IR, UV, and NMR spectroscopic measurements and other methods.^{41–46} MAO is mostly used in homogeneous solution, and for the best catalyst performance, a large excess is needed (Al/M molar ratios of 1000 are typical but they can reach 20000 in some cases). MAO reactivates inactive complexes of the type $\text{Cp}_2\text{M}-\text{CH}_2-\text{AlR}_2$ that were formed by hydrogen-transfer reactions.⁴⁷ Up to now the most favorable proposal for the active MAO species is to assume a cage built from six-membered rings which consist of MeAlO building blocks. In such cages there are monomeric AlMe_3 molecules that do the following job: alkylation of the metallocene dichloride complex and the formal abstraction of a methyl anion from the transition metal to give a metallocene monomethyl cation that is stabilized by a bulky MAO anion (Scheme 2).²⁴

Scheme 2. Model for an MAO Cage Stabilizing an Activated Metallocene Complex



The formal contact ion pair is the catalyst. This speculation is supported by the fact that other organoalumoxanes, like ethylalumoxane, are not suited as cocatalysts. Even if they can form cages, the corresponding monomeric aluminum triorganyls are too bulky to fit into these cages. The less the ion interactions, the better the catalyst's activity. Bulky ligands at the transition metal can indeed keep the MAO anion at a certain distance and produce a more or less "naked" metallocene monomethyl cation. As a consequence, the activity can be increased by factors of 5 or 6 (see section III.3.6, Figure 15).

Because of these circumstances, the high excess of MAO is demanded to provide sufficient MAO cages. It is interesting to note that the catalytically active share of MAO can be separated from the rest when a homogeneously activated metallocene catalyst is heterogenized by self-immobilization.^{12,48} In these cases, Zr/Al = 80 ratios were found.

Recently the authors invented another efficient, immobilized methylalumoxane cocatalyst: partially hydrolyzed trimethylaluminum (PHT) that proved to be different from common methylalumoxanes.⁴⁹ As a partial crystalline solid, PHT exhibits an octahedral environment for the aluminum atoms. PHT can be

used in connection with any imaginable support, and an Al/M ratio of 260 is sufficient for maximum activity.

II.3. Further Parameters

Besides complex and cocatalyst parameters, another category of parameters can play a major role during the catalytic reaction. The polymerization can be carried out in solution or heterogeneously as a slurry or gas-phase process with an immobilized catalyst.^{50–54}

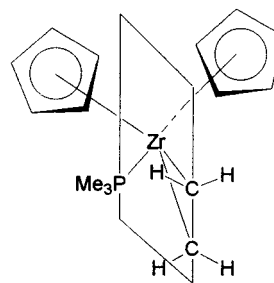
As the separation of the ion-pair catalyst \leftrightarrow cocatalyst mainly determines catalyst activities and polymer properties, the solvent plays an important role because it interacts with both the cation and the anion. Further, the solubility of the monomer and consequently the monomer concentration are very dependent on the solvent used.

The polymerization temperature, monomer concentration (pressure, solvent), and additives, like hydrogen, significantly affect catalyst activities, molecular weights of the formed polymer, as well as the stereoselectivity of the catalyst.^{55–57}

II.4. Reaction Mechanism and Stereoselectivity

Before we focus our attention on various catalyst parameters in order to tailor a "perfect catalyst", we have to study the reaction mechanism^{32,34,58–60} of the olefin polymerization in order to understand the influence of various parameters. It is obvious that the first step in the catalytic olefin polymerization is the coordination of the olefin to the Lewis-acidic metal center, which is confirmed by suitable model complexes such as $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2\text{C}_2\text{H}_4$ ⁶¹ or $\text{Cp}(\text{C}_5\text{H}_4\text{CMe}_2\text{C}_9\text{H}_7)\text{Zr}(\text{PMe}_3)$.⁶² The olefin ligand is coordinated with the C=C double bond axis lying in the plane that bisects the metallocene PMe_3 fragment (Scheme 3).

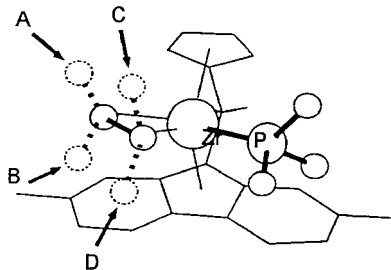
Scheme 3. Configuration of $\text{Cp}_2\text{Zr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$



The situation changes as soon as we deal with prochiral olefins such as propylene and when a center of asymmetry has to be considered. Then four different coordination modes (A–D) are possible for a prochiral olefin (Scheme 4).

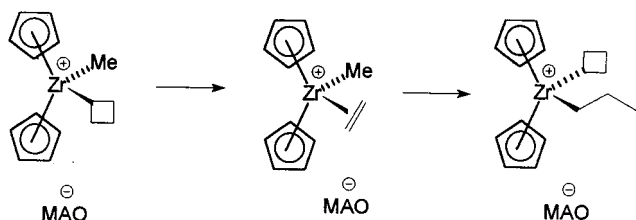
The alternatives A–D are all different in energy, and the favored species should be the one with the energy minimum. To achieve high stereospecificity, the energy gap between the favored species and the three competitors should be sufficiently high. NOE difference NMR spectroscopy of a suitable model compound gives evidence that position A is favored at room temperature.⁶³

Scheme 4. Coordination Possibilities for a 1-Olefin in the Complex
 $(C_5H_4-CMe_2-C_{13}H_6Me_2)Zr(PMe_3)(1\text{-olefin})$



The chain propagation proceeds with a formal ethylene insertion into the metal–carbon bond and the subsequent coordination of the next olefin molecule (Scheme 5).³⁰

Scheme 5. Propagation Step in the Polymerization of Ethylene



The insertion step consists of an alkyl migration to the olefin ligand; at the same time, a new free coordination site is generated at the vacant position of the former alkyl ligand. A catalyst molecule with a center of asymmetry (C_s symmetry) at the metal is predestinated to produce syndiotactic polypropylene: a catalyst with C_2 symmetry, isotactic polypro-

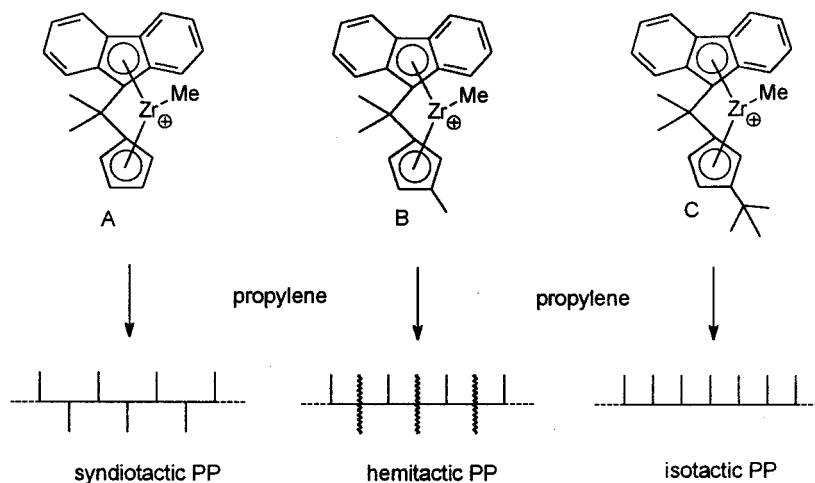
pylene (Scheme 6). If there is only a small or no energy difference in the various configurations of the coordinated prochiral olefin, atactic polypropylene will be formed. If this chain migration is blocked with a bulky substituent (C), the polymer chain cannot undergo this inversion step (“stationary” insertion) and as a consequence an originally syndiospecific catalyst (A) switches to an isospecific catalyst (C). A smaller, less bulky substituent (B) leads to a catalyst precursor that produces hemitactic polypropylene, which exhibits a random configuration on every second monomer unit.^{64–66}

Also, the chain end of the growing polymer can control the stereochemistry of the polymerization, as demonstrated by Ewen: Cp_2TiPh_2/MAO as a catalyst produces isotactic polypropylene.⁶⁷

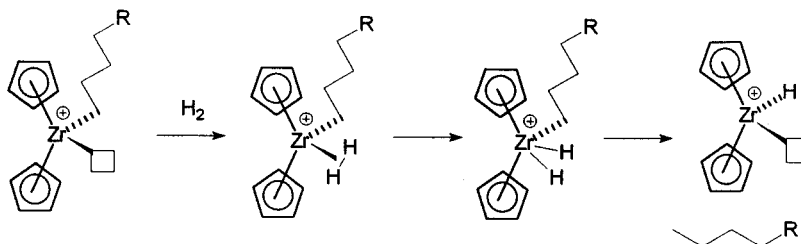
II.5. Chain Termination and Transfer

Another mechanism can have a tremendous influence on the nature of the polymer: the main chain termination pathway is a β -hydrogen transfer reaction to the monomer that produces a terminal olefin function at the end of the polymer chain. This long-chain terminal olefin can participate in further coordination steps. As a consequence, long-chain branching occurs. The degree of these copolymerization reactions depends on the nature of the corresponding catalysts. In a similar manner, the addition of hydrogen (Scheme 7) to the polymerization mixture can cause a dramatic increase in catalyst activity and a decrease in the molecular weight of the produced polyolefin. Molecular hydrogen can compete with the olefin for the free coordination sites. Presumably, hydrogen coordinates to the metal center and dihydrido complexes are formed as intermediates to

Scheme 6. Syndiospecific, Hemispecific, and Isospecific Metallocene Catalysts



Scheme 7. Proposal for the Reaction of the Catalyst with Hydrogen



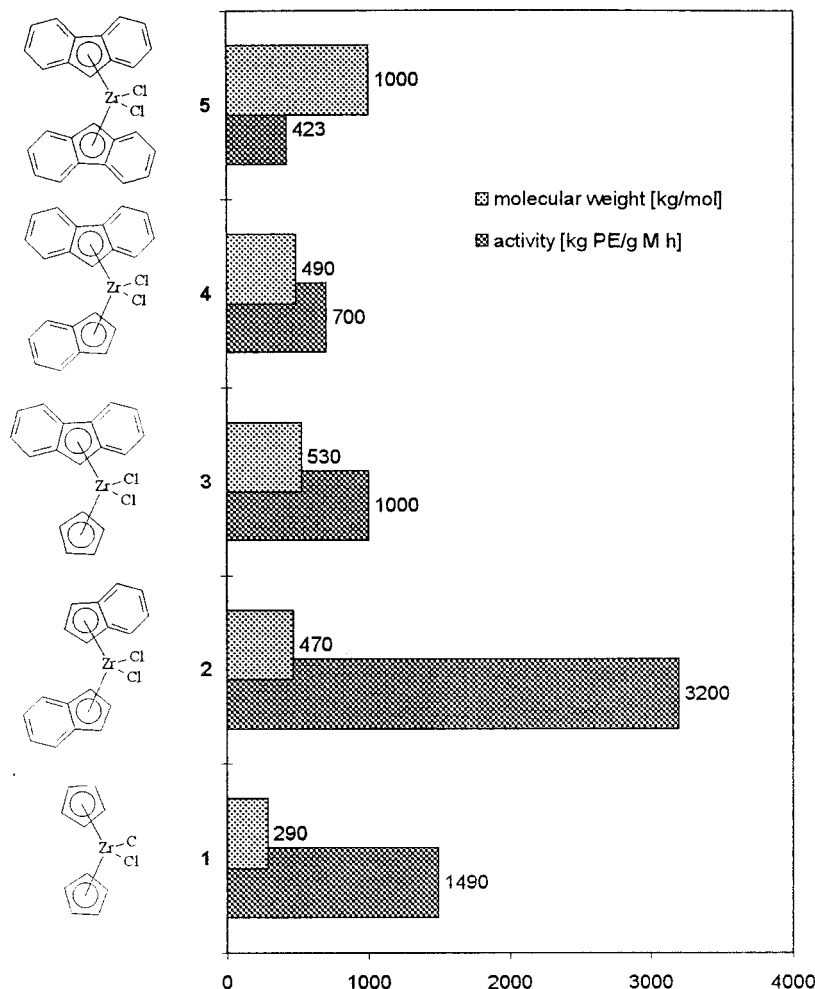


Figure 1. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$. Complexes **1**, **2**, **4**: MAO, Al/Zr = 1000. Complexes **3**, **5**: MAO/SiO₂, Al/Zr = 2500. Solvent: *n*-pentane; 10.0 bar ethylene pressure.

facilitate the elimination of a saturated alkane (polymer chain) and to produce a new coordination site. The formation of a metal–hydrogen bond allows further olefin insertion and chain growth without the loss of an active site.⁶⁸

Besides the β -H elimination mechanism, chain transfers to aluminum and to the monomer can occur. Also, β -alkyl abstraction has to be considered. The homolytic cleavage of the transition metal–carbon σ -bond should only play a minor role (decomposition of the catalyst).

III. The Influence of Structure Parameters on Catalyst Properties for Ethylene and Propylene Polymerization

III.1. General Considerations

All these aspects contribute to the “character” of a metallocene catalyst. Many attempts have been made in the past to design catalysts by molecular modeling. The results were not very satisfying because there are still too many open parameters that must be considered such as the degree of activation of the catalyst precursor, the interaction between catalyst cation and cocatalyst anion, or the role of the solvent. Because of this situation, we preferred the empirical way. The author’s group synthesized over 650 met-

allocene and half-sandwich catalyst precursors in the past years in order to test their catalytic potential and to study the influence of various catalyst parameters on the properties of the resulting polymers. The observed tacticities from the polymerization of prochiral olefins such as propylene should help to gain more insight into the corresponding reaction mechanisms. We investigated the influence of several structural and physical parameters on the activity of selected catalysts and the properties of the formed polymers, such as the molecular weight. With the variation of the ligand framework, metallocene complexes of group IV metals exhibit a very different potential in the polymerization of olefins. For better orientation, the catalyst precursors were divided into two major classes: unbridged metallocene complexes and bridged metallocene complexes. In each section the influence of the ligand nature (Cp = cyclopentadienyl, Ind = indenyl, or Flu = fluorenyl) and various substituents at these ligands on the catalytic properties under defined conditions is described and discussed in a short comparison. The amount of cocatalyst MAO can have a strong influence on the activities of the various catalysts.

In this study we did not incorporate the experimental results of other research groups. We do not want to ignore these results, but we cannot use them

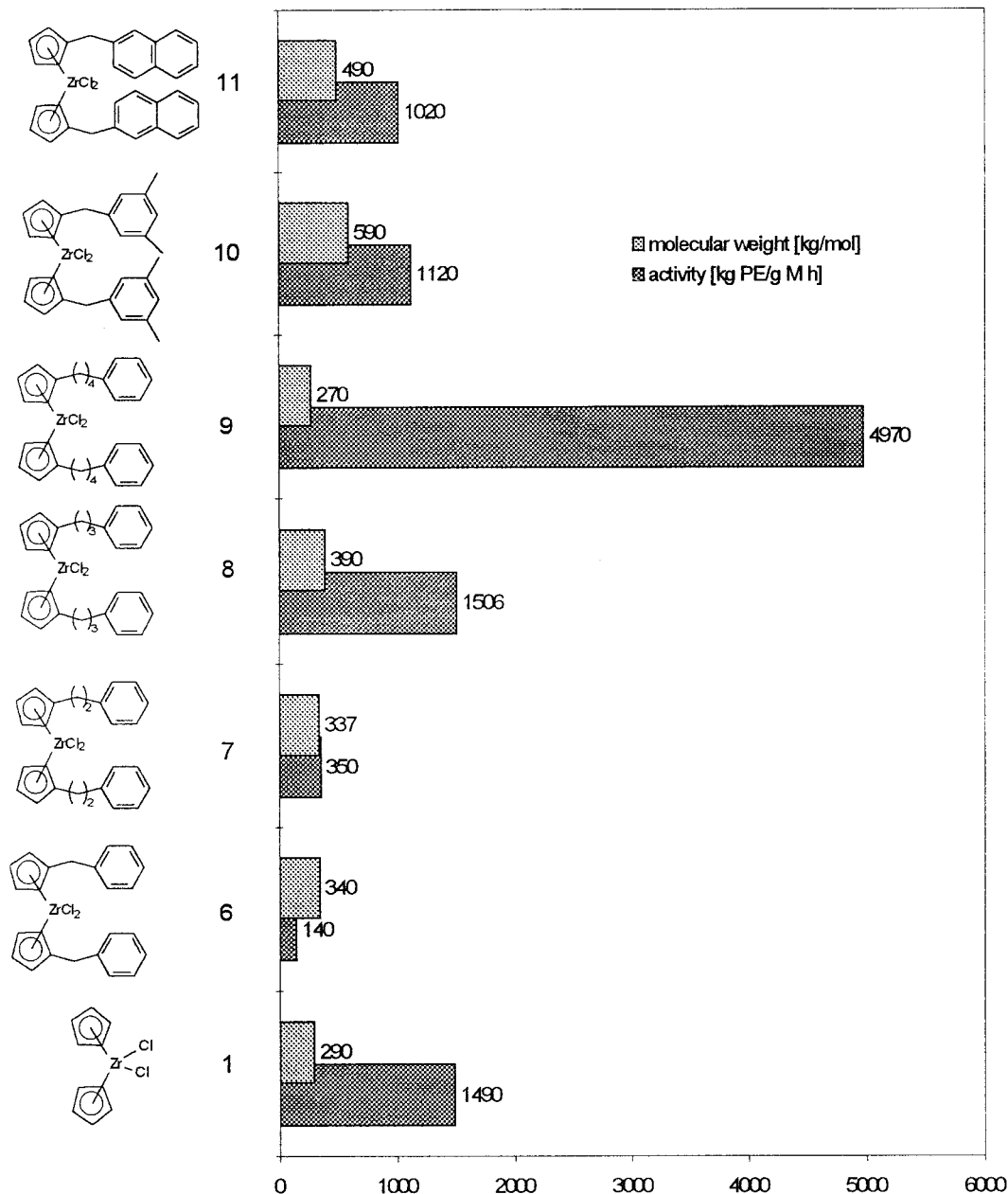


Figure 2. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000 (1), 3000 (6–11); solvent *n*-pentane; 10.0 bar ethylene pressure.

for a direct comparison because the polymerization conditions or other parameters were different from ours.

III.2. Unbridged Metallocene Complexes

III.2.1. The Nature of the Ligand in Complexes of the Type $(L^1)(L^2)ZrCl_2$ ($L^1, L^2 = Cp, Ind, Flu$)

Unbridged metallocene dichloride complexes exhibit maximum activities when cyclopentadienyl or indenyl ligands (3200 kg of PE/g of Zr·h) are used (Figure 1). As soon as fluorenyl ligands are involved, the catalyst activity drops (423 kg of PE/g of Zr·h). This behavior could be due to the potential of fluorenyl ligands for ring-slippage reactions, forming unstable complexes.¹¹ This instability is already obvious in the case of the unactivated metallocene dichloride complexes: whereas Cp_2ZrCl_2 can be stored

at air, Flu_2ZrCl_2 decomposes easily.⁶⁹ These ring-slippage reactions, where the fluorenyl ligand can coordinate to the central metal via an η^1 , η^3 , or η^5 bond, were intensively studied by means of NMR spectroscopy and X-ray analysis.^{70–73} Due to their bulky nature, fluorenyl ligands suppress the chain-terminating β -H elimination reaction resulting in high molecular weight polyethylene.

Another dynamic intramolecular effect has to be considered when prochiral olefins such as propylene are polymerized: the intramolecular rotation of the indenyl ligands around the metal–ligand bond axis can change the symmetry of the corresponding metallocene complex (*rac* or *meso*) continuously (“oscillating catalysts”^{74–77}) and thus produce polymers with isotactic and atactic blocks (Scheme 8) that are elastomeric thermoplastics.⁷⁸ Recent studies⁷⁹ indicate that the resin composition is dominated by the

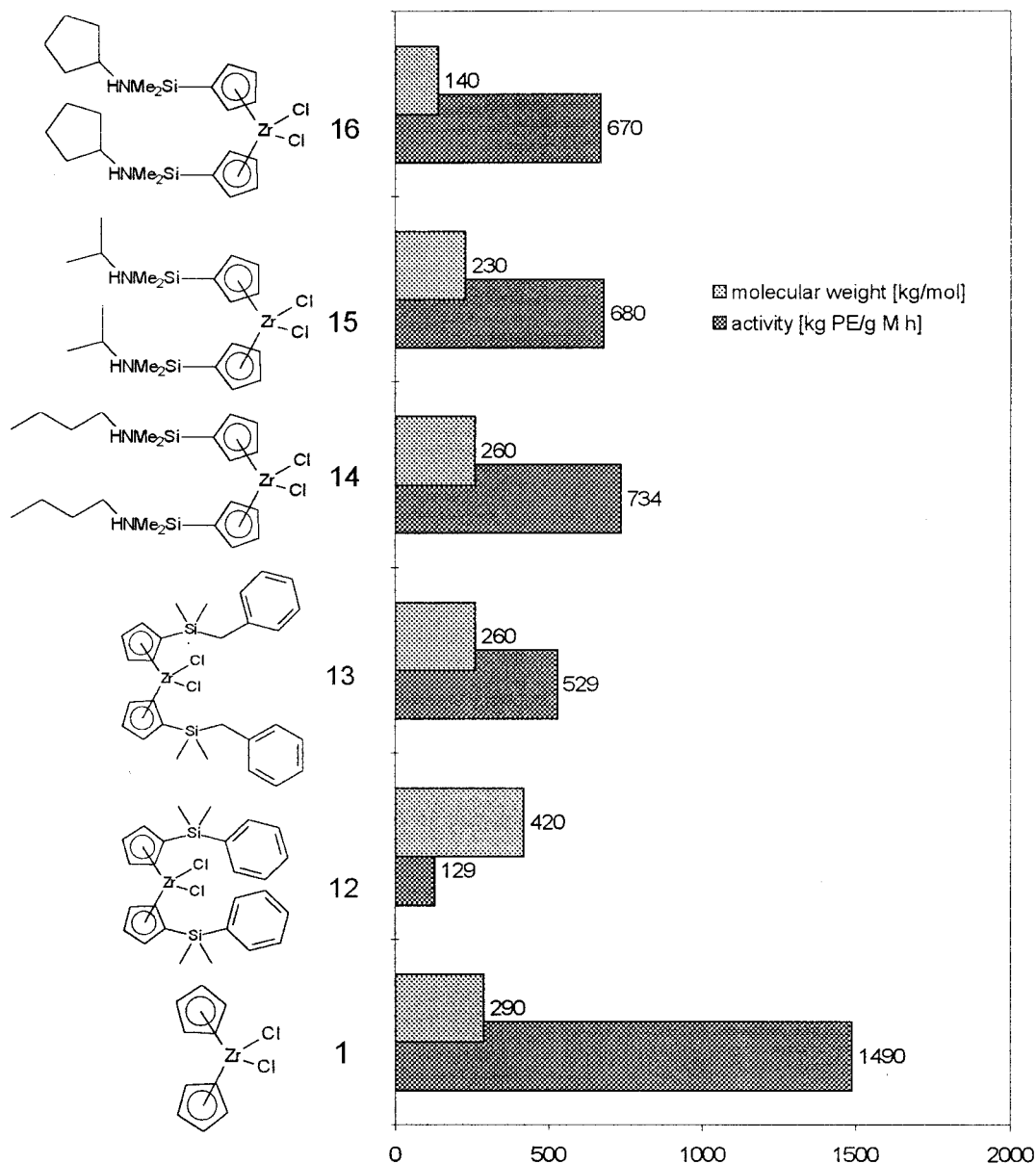
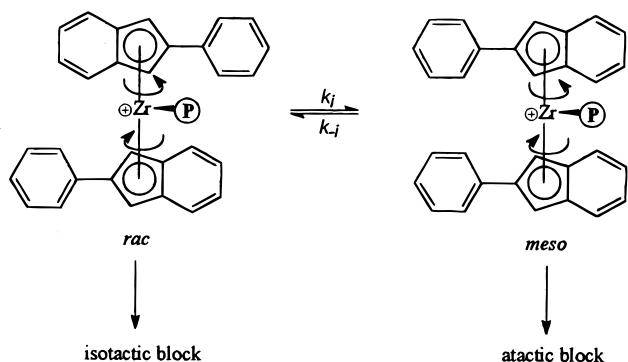


Figure 3. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 3000 (**12**, **13**), 5000 (**14**–**16**); solvent *n*-pentane; 10.0 bar ethylene pressure.

Scheme 8. "Oscillating Catalysts"



polymerization properties of the individual rotamers (*rac* and *meso*) rather than by the rate of "oscillation". The nature of the substituent on the indenyl ligand can have a strong influence on the material parameters (isotacticity: 7–37%).⁸⁰ Bulky substituents extend the lifetime of a special symmetry with the

consequence of formation of longer blocks. A temperature increase leads to shorter block lengths. The same result is observed when the propylene concentration is decreased. It is interesting to note that terminal olefin functions at the indenyl substituents do not allow "self-immobilization"^{12,48,81,82} of such complexes.⁸³ Obviously the olefin moiety is moving so fast during the rotation that it does not have the chance to coordinate to a metal.

III.2.2. Alkyl Substituents R with Terminal Aryl and Naphthyl Groups in Complexes of the Type $(C_5H_4R)_2ZrCl_2$

Alkyl substituents on cyclopentadienyl ligands usually have a positive influence on the activity of the corresponding metallocene catalysts. In this study (Figure 2), a series of complexes with alkyl substituents containing terminal aryl or naphthyl groups are presented.⁸⁴ The chain length of the substituent determines the activity of the catalyst to a very high extent. One explanation for this behavior might be

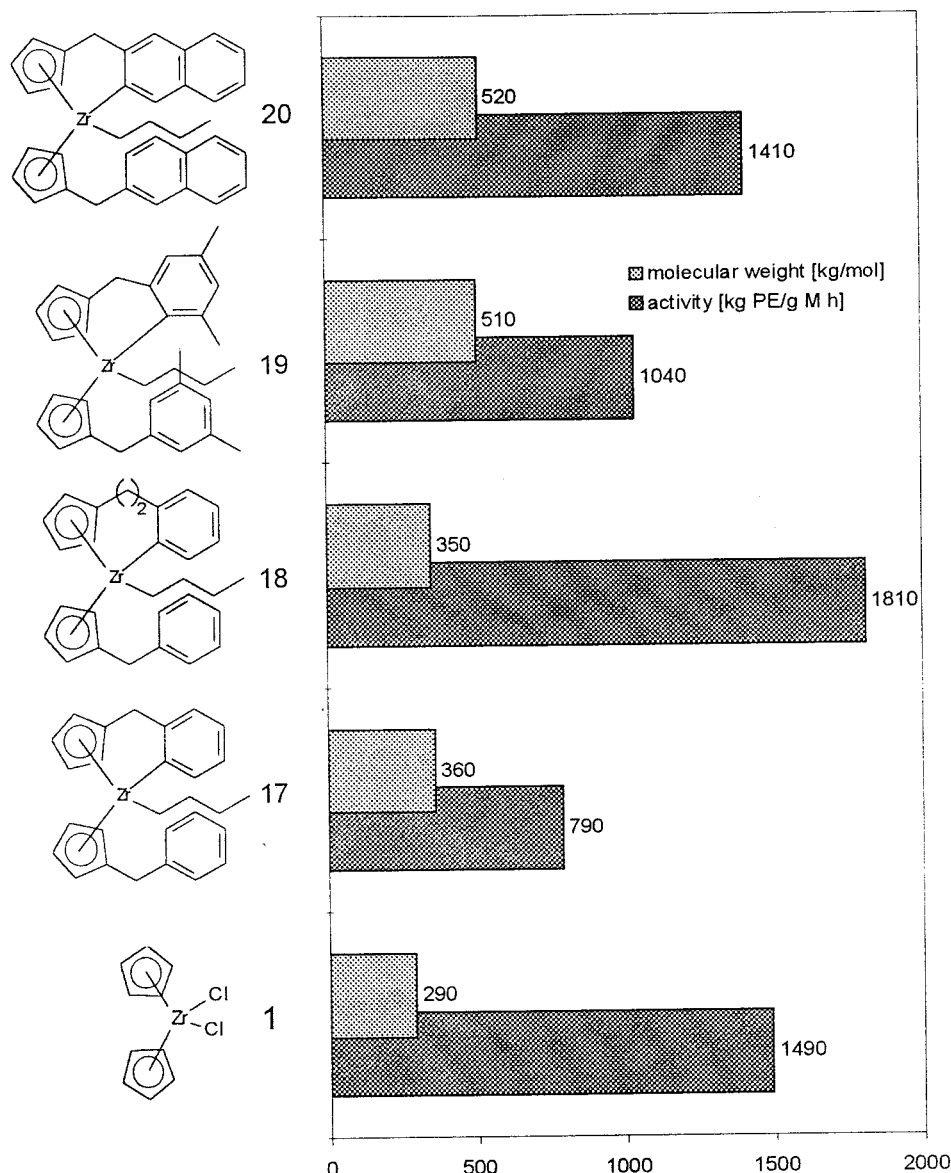


Figure 4. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 3000; solvent *n*-pentane; 10.0 bar ethylene pressure.

better separation of the catalyst cation and the MAO anion during the polymerization process. However, an interaction of the aromatic end group of the substituent with the Lewis-acid center of the catalyst could also be responsible for such an effect. Recently it has been demonstrated⁸⁵ that cationic complexes of the type $[(C_5H_5)(C_5H_4-CMe_2C_6H_5)ZrMe]^+ [RBC_6F_5_3]^-$ indeed show an interaction of the terminal aryl group and the metal.

III.2.3. Silyl Substituents with Terminal Phenyl Groups in Complexes of the Type $(C_5H_4silyl)_2ZrCl_2$

A Si₁ bridge in *ansa* metallocene complexes often increases the activity of a metallocene catalyst in comparison to its C₁-bridged derivative.⁸⁶ In compounds **12** and **13** (Figure 3), the silyl substituent on the cyclopentadienyl ligand has a disadvantageous influence on the activity compared to **1**. A convincing argument for this behavior is still missing.

III.2.4. Metallacyclic Bis(Cyclopentadienyl) Complexes

The monosubstituted bis(cyclopentadienyl) complexes of section III.2.2 form metallacycles^{87,88} when

they are reacted with butyllithium.⁸⁹ The catalytic activities of the metallacycles can be more than 5 times higher (**17**) than those of the corresponding unbridged metallocene dichloride precursors (**6**). The absence of any chlorine-containing components as catalyst poisons could be an explanation for this positive effect but also a different polymerization pathway (restricted chain migration "stationary mechanism"¹⁷) must be discussed (Figure 4).

III.2.5. Substituted Indenyl Ligands in Metallocene Complexes of the Type $(Ind')(Cp)ZrCl_2$ (Ind' = Substituted Indenyl)

In this series (Figure 5) the indenyl fragment is substituted with methyl and phenyl groups while the cyclopentadienyl ligand remains unchanged.⁹⁰ The maximum activities exceed those with substituted cyclopentadienyl ligands and therefore place some of these catalysts in the category "most active catalysts".

We have no convincing explanation for the high activity of complex **5**. No obvious trend in the molecular weights of the obtained polymers was found.

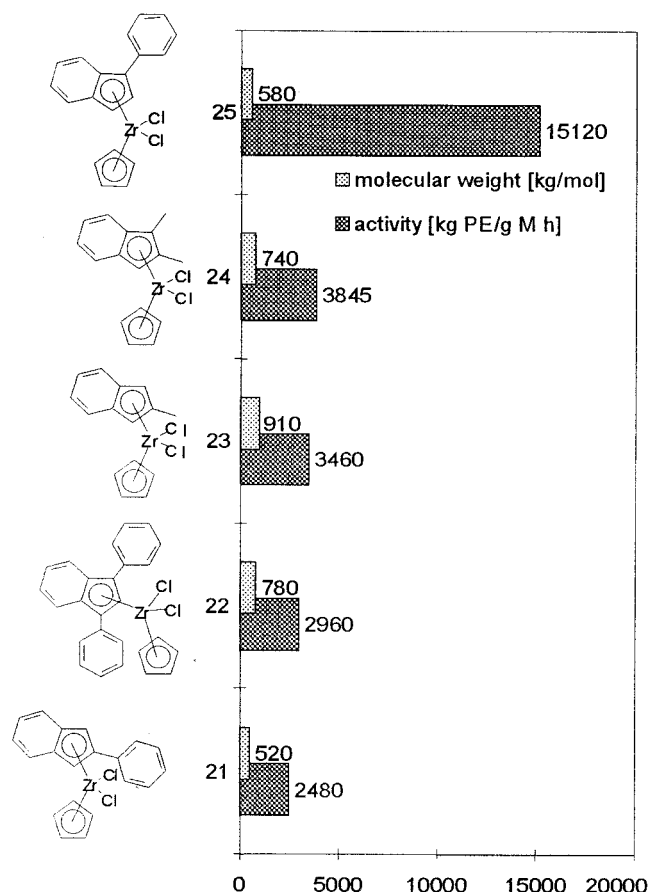


Figure 5. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; solvent *n*-pentane; 10.0 bar ethylene pressure.

III.2.6. Hydrido Tripyrazolyl Borate Ligands (Tp) Compared with Cp and Ind Ligands in Unbridged Complexes of the Type (Tp)(L)ZrCl₂ (L = Cp, Ind, Ind')

Hydrido tripyrazolyl borato ligands⁹¹ play a significant role in coordination chemistry as they formally act as cyclopentadienyl equivalents donating 6 electrons to a central metal. Despite this analogy, there are significant electronic and sterical differences between Cp and Tp ligands.^{92–94} The Tp anion proved to be a stronger electron donor and a more bulky ligand than the Cp anion, leading to more intensive protection of the central metal compared to the cyclopentadienyl system. A look at the polymerization results of these complexes reflects this situation (Figure 6): the activity drops tremendously when using a tripyrazolyl borato ligand instead of a cyclopentadienyl ligand. This is due to an electronically overloaded active metal center without enough Lewis acidity.

III.2.7. Methyl Substituents at Various Positions of the Fluorenyl Ligand in Complexes of the Type (Flu')(Cp)-ZrCl₂

Unbridged (fluorenyl)(cyclopentadienyl) metallocene dichloride complexes are potential catalyst precursors for the production of syndiotactic polypropylene. There are three prerequisites the catalyst precursors have to fulfill: *C_s* symmetry and a ligand ensemble with one ligand being much smaller (Cp) than the other (Flu). Moreover, the hindered rotation

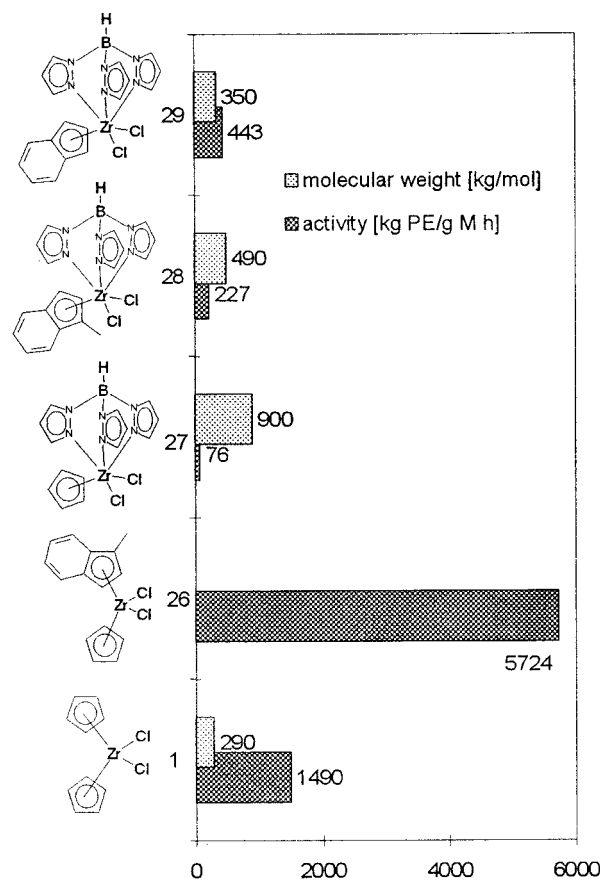


Figure 6. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; solvent *n*-pentane; 10.0 bar ethylene pressure.

of the π -ligands can be achieved by bulky substituents, preferably at the fluorenyl ligand. Despite these fulfilled complex conditions, these metallocene complexes produce atactic polypropylene⁹⁵ in small yields and therefore are not useful for a large-scale application. However, unbridged (fluorenyl)(cyclopentadienyl) metallocene dichloride complexes are excellent catalysts for the polymerization of ethylene. Figure 7 shows the influence of several methyl substituents at the fluorenyl ligand on the catalyst activity. Complexes **3** and **5** show the highest activities, probably due to hindered ring-slippage reactions with substituents at the fluorenyl positions 1 and 9.

III.2.8. Various Substituents at the Positions 2 and 7 of the Fluorenyl Ligand in Complexes of the Type (Flu')(Cp)-ZrCl₂ (Flu' = Substituted Fluorenyl)

Substituents at fluorenyl positions 2 and 7 are accessible in very good yields via one- or two-step reactions.⁹⁶ The highest activity in the polymerization of ethylene was achieved by complex **35** containing bulky *tert*-butyl substituents (Figure 8). Polar groups are unsuitable for good catalyst performance, e.g., methoxy or halide substituents (**36,37**), because the heteroatom acts as a Lewis base and blocks another metal center.

III.2.9. Various Substituents at Position 9 of the Fluorenyl Ligand in Complexes of the Type (Flu')(Cp)ZrCl₂

In general, aliphatic substituents enhance the activity of polyethylene catalysts. In this series of

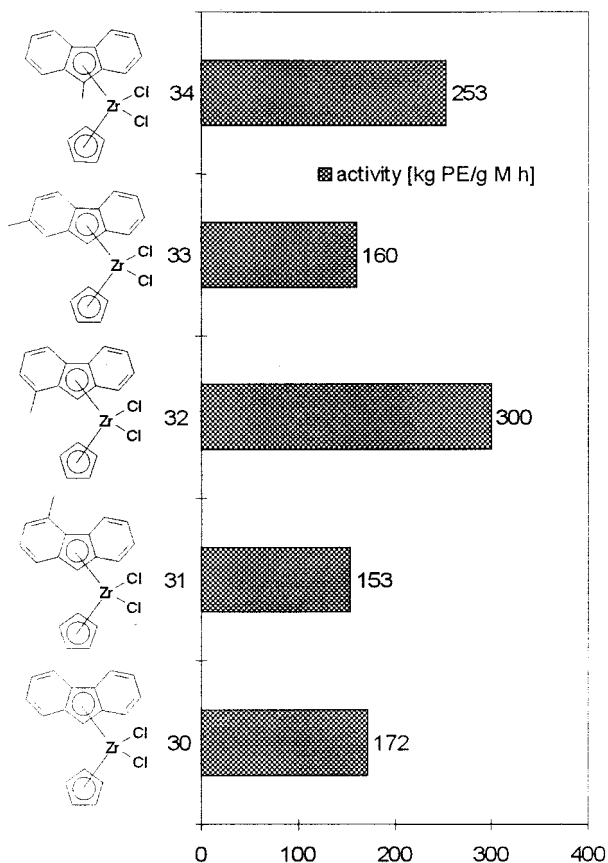


Figure 7. Polymerization conditions: $T_p = 10\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; solvent *n*-pentane; 10.0 bar ethylene pressure.

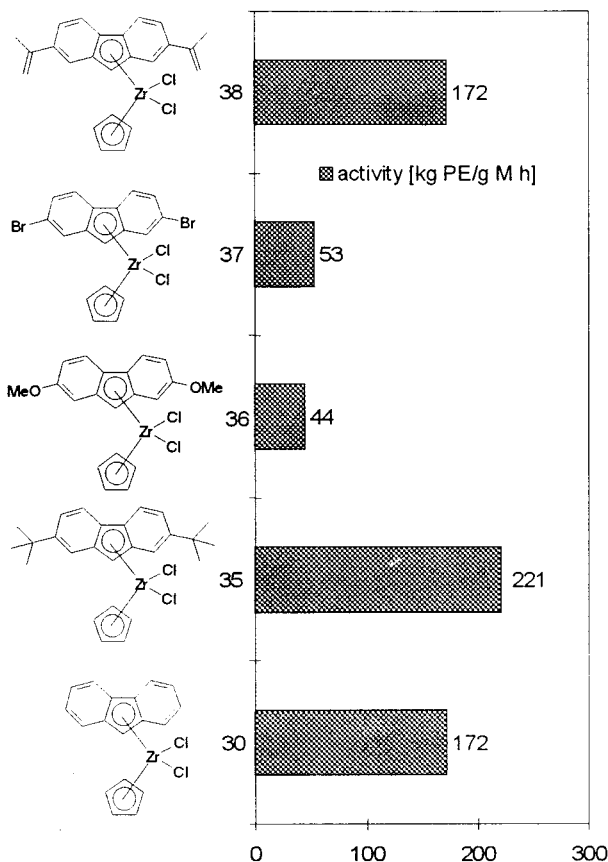


Figure 8. Polymerization conditions: $T_p = 10\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; solvent *n*-pentane; 10.0 bar ethylene pressure.

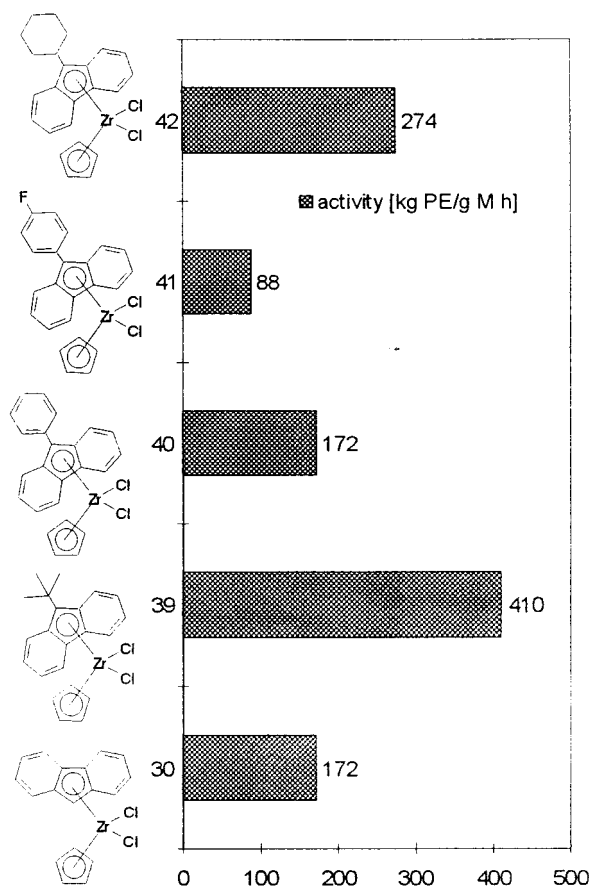


Figure 9. Polymerization conditions: $T_p = 10\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; solvent *n*-pentane; 10.0 bar ethylene pressure.

unbridged (fluorenyl)(cyclopentadienyl) zirconium dichloride complexes, the influence of substituents at position 9 of the fluorenyl ligand is described.⁹⁷ Bulky, aliphatic groups have a positive effect on the catalytic performance of this complex family, whereas aromatic substituents generally reduce the polymerization activity (Figure 9). Ring-slippage reactions are supposed to be the reason for this catalytic inefficiency.

III.3. Bridged Metallocene Complexes

III.3.1. Variation of the Bridging Unit in Metallocene Complexes of the Type (Flu-CRR-Cp)ZrCl₂

From the bridged metallocene complexes, the bis-(indenyl) derivatives must be considered as the pioneer compounds to produce isotactic polypropylene.^{4,98,99} At the former Hoechst company, this system was optimized and commercialized for high activity of the catalyst and high molecular weight (ca. 1 000 000 g/mol) and high isospecificity (98%) of the polymer.³

In this review, no *ansa* metallocene complexes with indenyl ligands are incorporated due to the already existing comprehensive literature.⁴ Furthermore, it would have been necessary to repeat all polymerization experiments with these complexes in order to obtain results for a comparison with the already established parameters.

For the syndiospecific polymerization of prochiral olefins, such as propylene, catalysts with C_s sym-

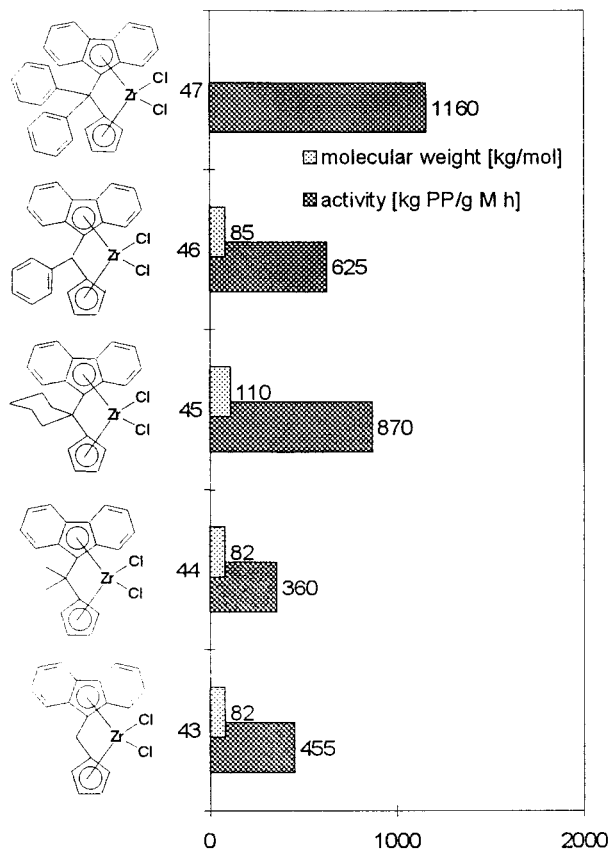


Figure 10. Polymerization conditions: $T_p = 10\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; bulk polymerization of propylene.

metry and a rigid ligand framework are required. The first metallocene catalyst that has met these prerequisites is Razavi's isopropylidene-bridged fluorenyl cyclopentadienyl zirconium dichloride complex **44**.^{16,100} In the complex series of Figure 10, several substituents are introduced into the bridging unit of that type of complexes, known to have a great influence on activity and stereospecificity.^{101–104} Indeed, bulky phenyl or cyclohexyl groups at the bridging unit increase the catalyst performance (**45–47**) and the molecular weight of the produced polypropylene.

III.3.2. Substituents at the Fluorenyl Fragment in *ansa*-Metallocene Complexes of the Type $(Flu-CMe_2-Cp)ZrCl_2$

Besides the bridging unit, the fluorenyl fragment offers many possibilities for the selective modification of the discrete complex structure by variation of type, number, and position of the substituents. The series shown in Figure 11 represents some selected complexes^{105,106} and the influence of various substituents on catalyst activity and molecular weight. All complexes produce, in combination with MAO, syndiotactic polypropylene with fairly good activities and low molecular weights except complex **49**, which almost reaches an activity of 900 kg of PP/g of Zr·h.

III.3.3. Other Metallocene Complexes that Produce Highly Syndiotactic Polypropylene

C_s symmetry is not an absolute prerequisite for syndiospecific metallocene catalysts: despite its symmetry violation, complex **55** (Figure 12) provides

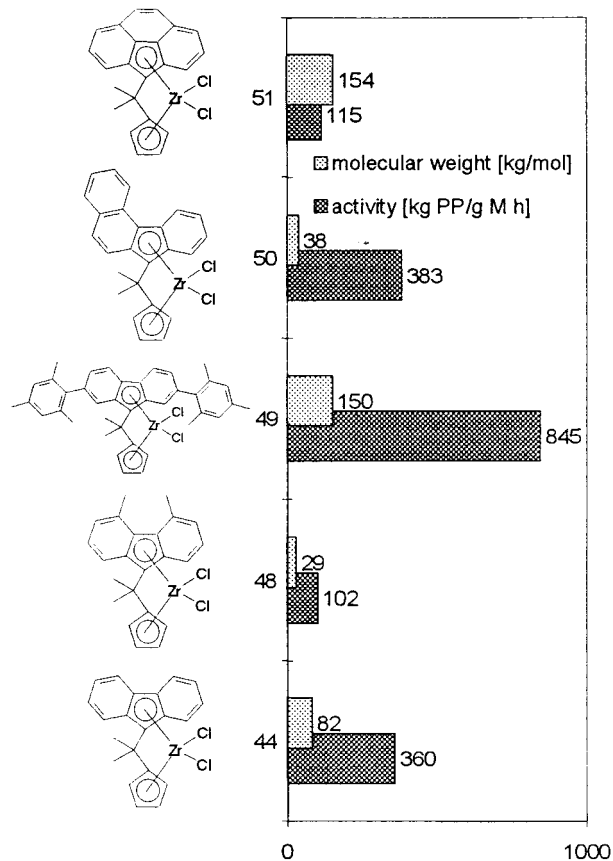


Figure 11. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 1000; bulk polymerization of propylene.

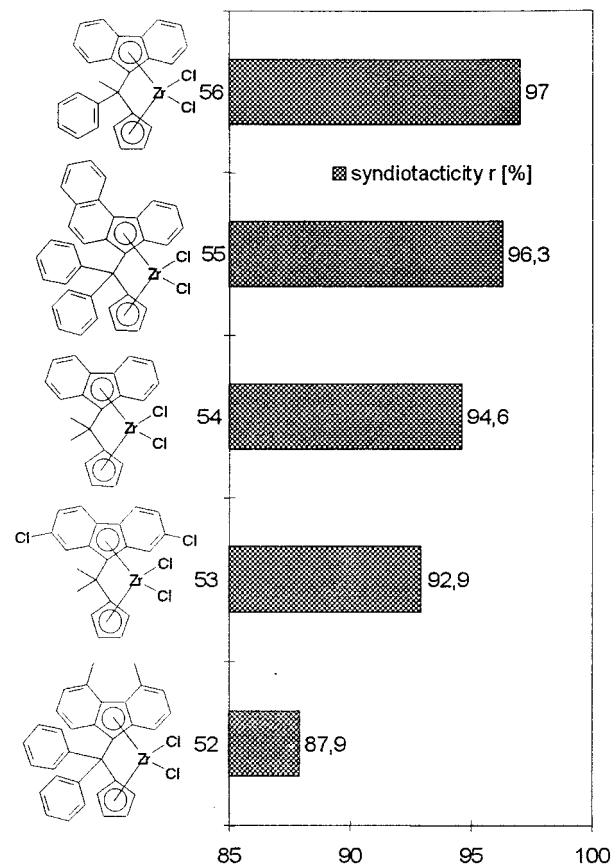


Figure 12. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 2000; bulk polymerization of propylene.

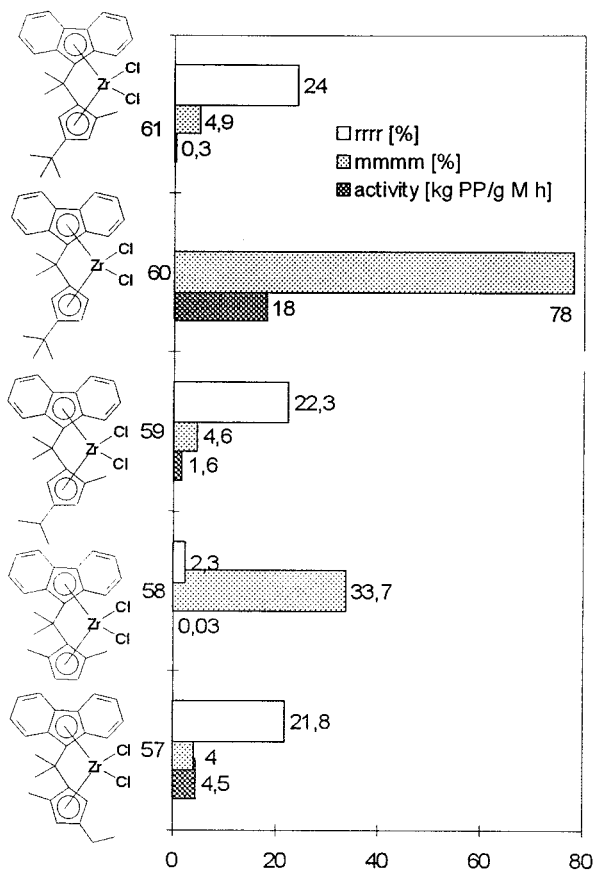


Figure 13. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; $\text{Al/Zr} = 1500$; bulk polymerization of propylene.

highly syndiotactic polypropylene with a total of *r*-sequences of 96.3%. Complex **52** represents a special case: a very low activity is combined with low syndiospecificity. The X-ray analysis¹⁰⁶ of the similar complex **48** ($r = 77\%$) (Figure 11) gives a closer look at the molecular conditions at the central metal in 4,5-dimethylated *ansa*-fluorenyl cyclopentadienyl complexes: the steric repulsion of the two methyl substituents forces one methyl group into the direct sphere of influence of the central metal, thereby hindering an ideal coordination of the next olefin. This results in low activities and stereospecificities.

III.3.4. Substituents at the Cyclopentadienyl Fragment in *ansa*-Metallocene Complexes of the Type $(\text{Flu}-\text{CMe}_2-\text{Cp}^*)\text{ZrCl}_2$

In the course of the detailed investigation of *ansa*-(fluorenyl)(cyclopentadienyl) metallocene complexes and their catalytic potential, substituents at the cyclopentadienyl fragment have been of major interest. Earlier publications only describe single substitutions at the cyclopentadienyl fragment leading to a change in tacticity¹⁷ of the produced polypropylene (Figure 13). Methyl substituents at position 2 of the cyclopentadienyl ligand increase the syndiospecificity of a metallocene catalyst¹⁰⁷ (**57,61**) as long as there is no second methyl substituent present at position 5 of the cyclopentadienyl fragment (**58**).

III.3.5. Fused Ring Systems in Complexes of the Type $(\text{Flu}'-\text{C}_2\text{H}_4-\text{Flu}')\text{ZrCl}_2$

Bridged *ansa*-bis(fluorenylidene) zirconium dichloride complexes with fused ring systems^{108,109} have

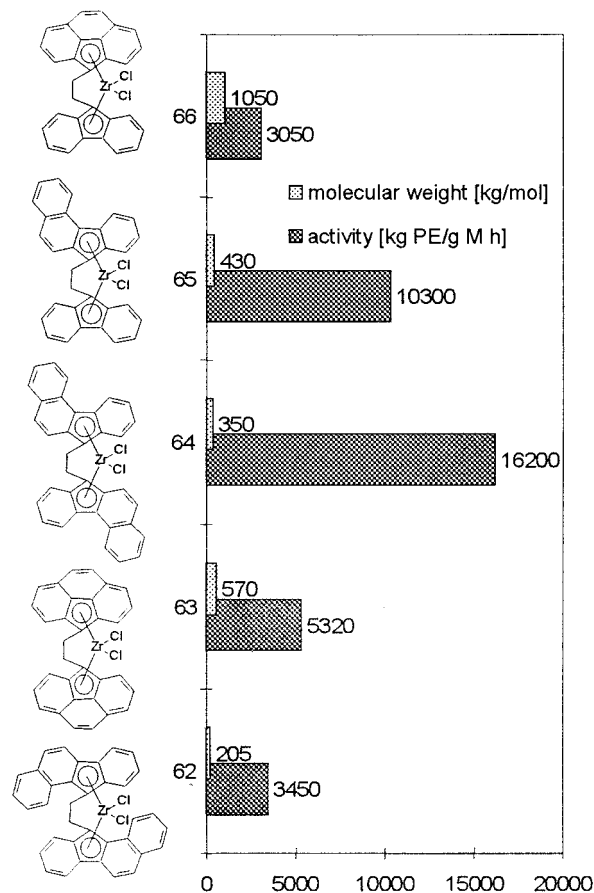


Figure 14. Polymerization conditions: $T_p = 40\text{ }^\circ\text{C}$; MAO/SiO_2 , $\text{Al/Zr} = 2500$; solvent *n*-pentane; 10.0 bar ethylene pressure.

proved to be very active in combination with MAO for the polymerization of ethylene (Figure 14). Complexes with benzo[*c*] or dibenzo[*c,c'*] fluorenyl derivatives are supposed to provide the highest activities for the polymerization of ethylene due to the enhanced separation of the corresponding catalyst cation and the MAO counteranion which is generated in the activation process. Whereas we did not succeed in the synthesis of the dibenzo[*c,c'*] fluorenyl derivative, the monosubstituted benzo[*c*] derivatives **64** and **65** exhibit, as predicted, a very high activity in the polymerization of ethylene, placing complex **64** at least into the "top 10" of the most active catalysts known so far.

III.3.6. The Position of Methyl Substituents in Complexes of the Type $(\text{Flu}'-\text{C}_2\text{H}_4-\text{Flu}')\text{ZrCl}_2$

The influence of methyl substituents at the fluorenyl ligand in *ansa*-bis(fluorenylidene)zirconium dichloride complexes¹² on the catalytic performance has been of further interest. The fluorenyl positions 4 and 5 are directly located at the active center and therefore have an important effect on the catalyst activity but are supposed to have less effect on the molecular weight of the formed polymer due to their nonbulky nature (Figure 15). Indeed, methyl substituents at position 4 or 5 at the fluorenyl fragment dramatically increase the catalytic activity of these metallocene complexes. As already discussed in the previous section, these substituents obviously pro-

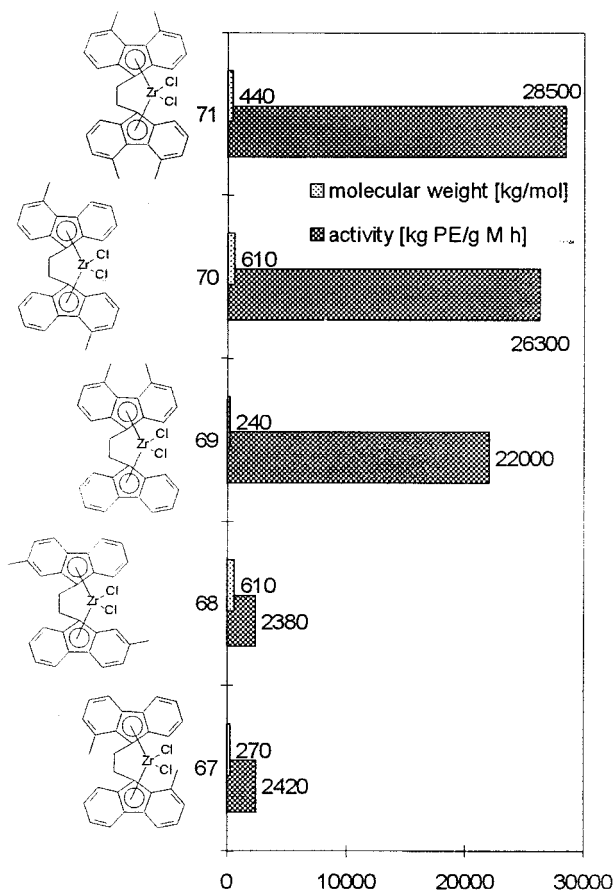


Figure 15. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 20000; solvent *n*-pentane; 10.0 bar ethylene pressure.

mote the separation of the active catalyst–cocatalyst ion pair generating a very Lewis-acidic metal center. In the case of the polymerization of propylene (see section III.3.2), these methyl substituents in *ansa*-(fluorenyl)(cyclopentadienyl)zirconium dichloride complexes decrease the activity due to a sterical hindrance of the entering monomer unit. All other positions for methyl substituents are not favored and decrease the catalytic performance of these catalysts.

III.3.7. Variation of the Bridging Unit in *ansa*-Bis-(Fluorenylidene) Complexes of the Type (Flu-X-Flu)ZrCl₂

The bridging unit of *ansa*-bis(fluorenylidene)zirconium dichloride complexes^{15,110,111} (Scheme 9) has an important influence on the catalytic properties of these complexes. The direct effect of the bridging atoms on the "bite angle" (calculated with MM2 methods) clarifies this situation (Figure 16). A bigger

Scheme 9. Dependence of Bite Angle on Bridging Moiety

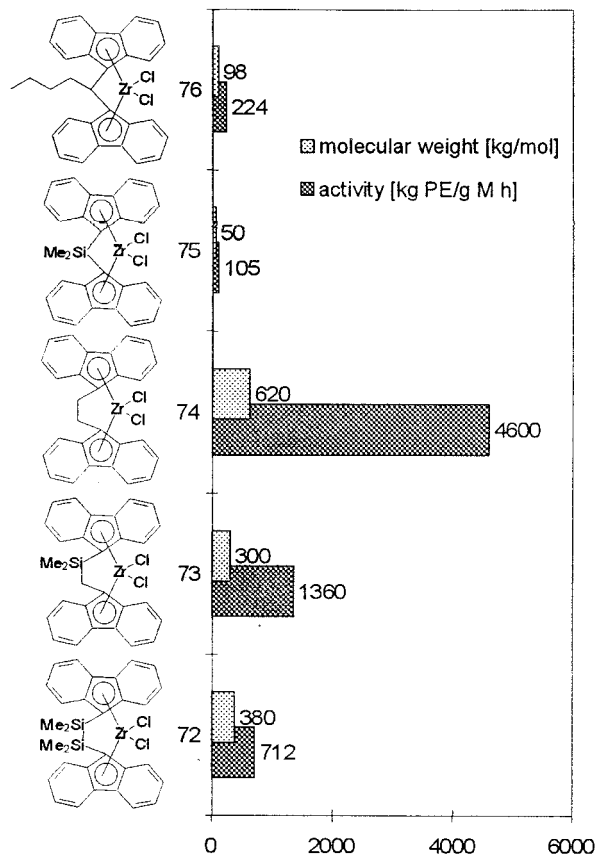
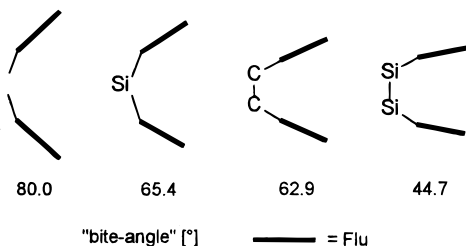


Figure 16. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 20000; solvent *n*-pentane; 10.0 bar ethylene pressure.

bite angle is supposed to increase the catalyst activity because of an unforced monomer entrance. However, electronic influences also have to be considered. The highest activities have been obtained in the case of the C₂ (74) and SiC (73) bridged *ansa*-bis(fluorenylidene) complexes, which obviously combine the thermal stability with ideal electronic and sterical conditions.

III.3.8. Variation of the Substituent R in Bis(silylene)-amido-Bridged Metallocene Complexes of the Type (Cp-SiMe₂-NR-SiMe₂-Cp)ZrCl₂

The synthesis of these bis(silyl) amido-bridged bis-(cyclopentadienyl) complexes of group IV metals succeeds by monolithiating the cyclopentadienyl dimethylsilyl amido ligand precursor with *n*-BuLi followed by the subsequent reaction with MCl₄.^{112,113} In combination with MAO, these catalysts exhibit high polymerization activity with molecular weights of the produced polymer ranging from 320 to 750 kg/mol (Figure 17). The Lewis-basic nitrogen atom is deactivated by two neighboring dimethylsilyl groups and therefore cannot interact with the cationic Lewis-acidic center of another catalyst molecule. The lowest activity has been achieved with complex 77 containing an ω -methoxy group at the bridge; this polar group has already proved to be unsuitable for effective polymerization catalysts even if bonded at a fluorenyl unit (see section III.2.8).

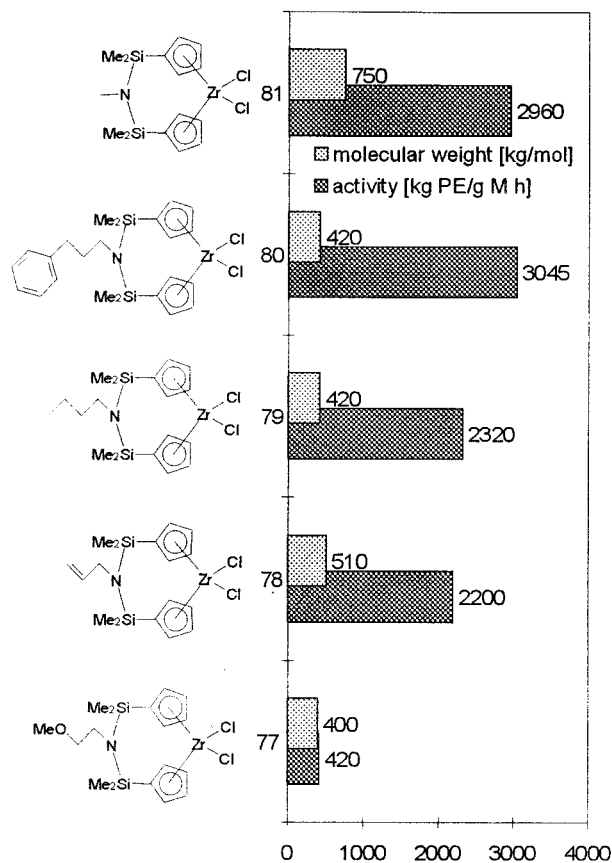


Figure 17. Polymerization conditions: $T_p = 60\text{ }^\circ\text{C}$; MAO, Al/Zr = 20000; solvent *n*-pentane; 10.0 bar ethylene pressure.

IV. Conclusions

What did we learn? We have to confess that we still do not understand all details in order to be able to predict the exact properties of a designed metallocene catalyst. Too many parameters are involved that determine the kinetics of the polymerization. Tiny changes at the metallocene complex can have a drastic effect on the activity of the catalyst and the properties of the polymers. Even molecular modeling cannot answer all the questions; it only can confirm trends. Nevertheless, the presented empirical trends should be helpful to prepare more or less tailored metallocene catalysts for application.

Another aspect that can have a severe influence on the catalytic properties has not even been mentioned so far: the heterogenization of these homogeneous catalysts for industrial application in order to avoid "fouling" in the reactor. This topic is discussed in a separate contribution of this issue (G. Fink et al.).

This section gives a summarized, comparative overview of remarkable catalyst or polymer properties in homogeneous solution, independent of the complex family or polymerization conditions.

IV.1. Top 5 of the Most Active Metallocene Complexes for Ethylene Polymerization

(4,4',5,5'-Tetramethyl)bis(fluorenylidene)(1,2-ethylidene)zirconium dichloride (**71**) represents the most

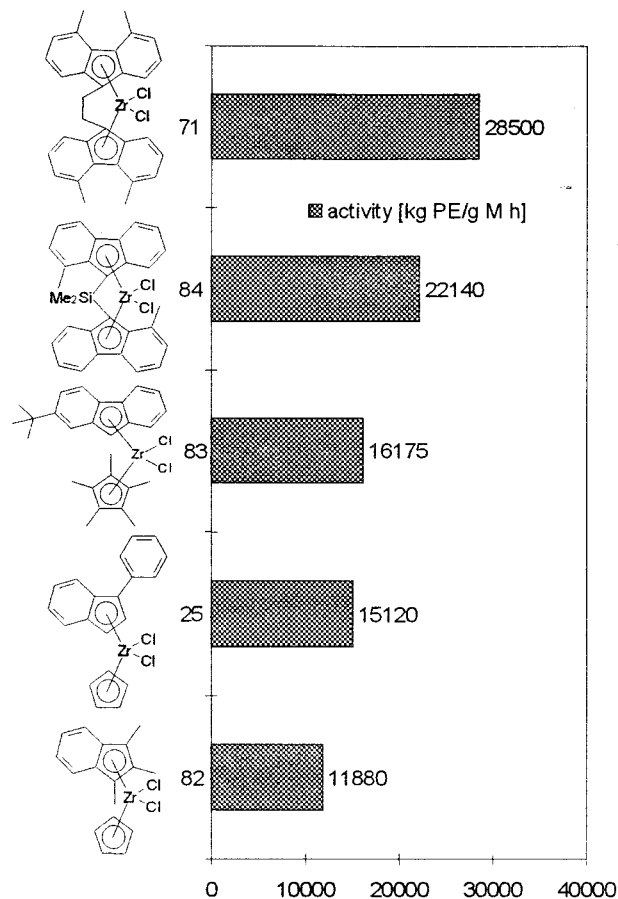


Figure 18. Polymerization conditions: $T_p = 60$ (**82**, **71**), 30 (**25**, **84**), $10\text{ }^\circ\text{C}$ (**83**); Al/Zr = 20000 (**71**), 8000 (**84**), 1000 (**82**, **25**, **83**); solvent *n*-pentane; 10.0 bar ethylene pressure.

active metallocene dichloride complex under these polymerization conditions that has ever been published. All methyl substituents are in direct contact with the active catalyst center, thus increasing the distance between the cationic metal center and the anionic MAO cocatalyst. The thermal stability and ideal electronic and sterical conditions make the *ansa*-bis(fluorenylidene) complexes **71** and **84** the most active catalysts for the polymerization of ethylene. This high catalytic performance has to be paid with a huge excess of MAO (Al/Zr = 20 000) and strong reactor fouling during the polymerization process. Lowering the MAO excess to Al/Zr = 2500 leads to a dramatic decrease in polymerization activity: the catalyst precursor 1,2-bis(fluorenylidene)-ethylidenezirconium dichloride loses 97% (4600–120 kg of PE/g of Zr·h) of its polymerization activity. More effective at lower Al/Zr molar ratios and also at a lower temperature level are unbridged, sterically protected cyclopentadienyl complexes of zirconium (**25**, **82**, **83**) representing the second class of highly active metallocene complexes (Figure 18).

IV.2. Metallocene Complexes with Low Activity

A low catalyst activity (Figure 19) in the polymerization of α -olefins with metallocene and half-sandwich complexes can be due to many reasons: the central metal plays the most important part in

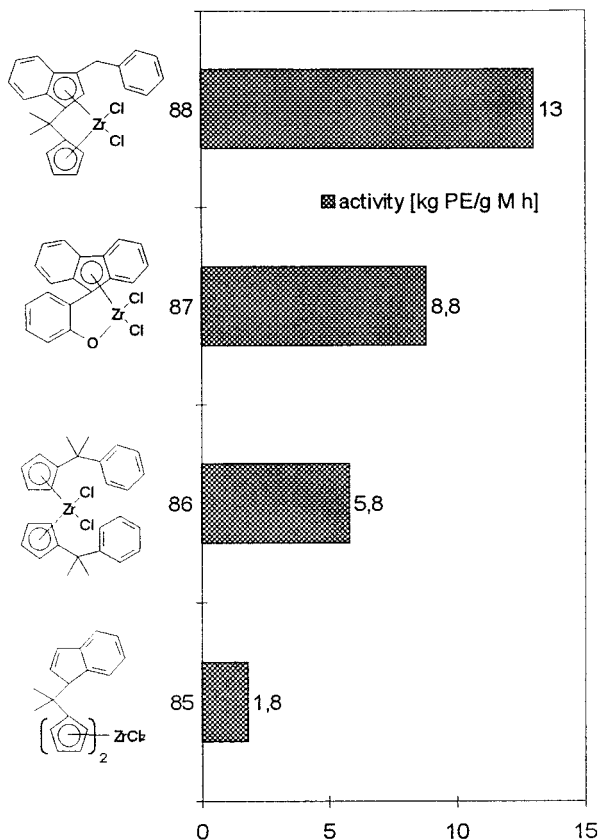


Figure 19. Polymerization conditions: $T_p = 60$ °C; MAO, Al/Zr = 1000 (**87**), 3000 (**85**, **86**, **88**); solvent *n*-pentane; 10.0 bar ethylene pressure.

Ziegler–Natta-type catalysis. Depending on the used ligands, zirconium (see previous section) and in some cases titanium provide the highest polymerization activities. Hafnium, like other elements of the sixth period, exhibits unattractive activities due to kinetic reasons (slow olefin coordination and insertion step). However, most hafnium complexes provide polymers with higher molecular weights than the analogous zirconium or titanium complexes due to thermodynamically stronger Hf–C bonds.

Steric effects, such as the bite angle between the two η^5 -coordinated aromatic ligands or bulky substituents at these ligands (**85**–**88**), dramatically influence the catalytic performance.

In addition, the electronic structure, mainly determined by the central metal and Lewis-basic or Lewis-acidic substituents at the ligands, is a considerable aspect for the polymerization activity of metallocene and half-sandwich complexes.¹¹⁴ Complexes with a sterically accessible oxygen or a nitrogen atom (Lewis bases) coordinated to the central metal are not useful for good catalytic performance. Generally, hafnium metallocene and half-sandwich complexes exhibit lower polymerization activities due to a more stable hafnium–carbon bond,¹¹⁵ which lowers the insertion rate of the coordinated monomer into the growing polymer chain.

Another aspect for low catalyst activity is its limited lifetime due to decomposition processes such as the reduction of the metal atom in the catalyst.

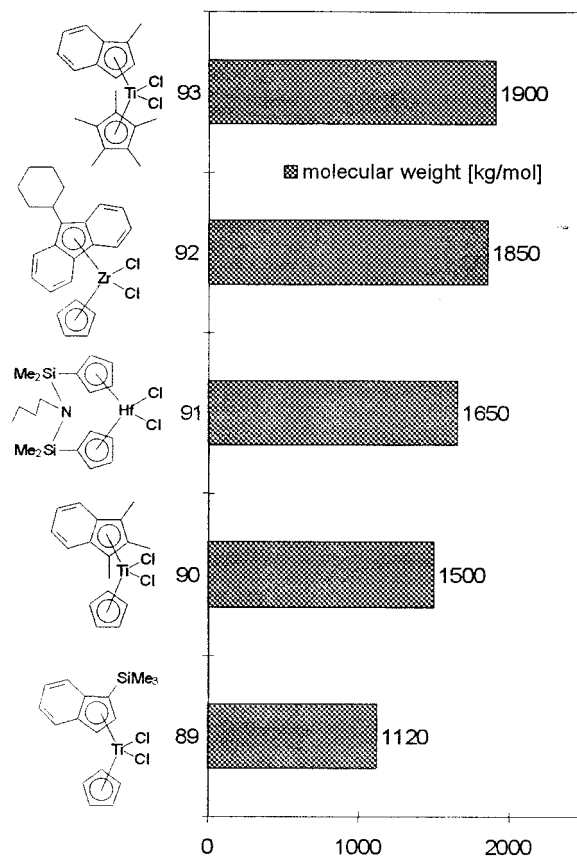


Figure 20. Polymerization conditions: $T_p = 60$ (**91**), 30 (**89**, **90**, **93**), 10 °C (**92**); Al/Zr = 5000 (**91**), 1000 (**89**, **90**, **92**, **93**); solvent *n*-pentane; 10.0 bar ethylene pressure.

IV.3. Metallocene Complexes that Produce High Molecular Weight Polyethylenes

In many cases high molecular weight polyethylene is produced by catalysts with bulky substituents in the ligand sphere (**89**, **90**, **92**, **93**). One interpretation could be that these substituents partially block the free coordination site that is necessary for the chain transfer step via a β -hydrogen elimination reaction. Obviously, the Si–N–Si bridging unit in complexes of type **91** creates a unique bite angle at the active center that partially suppresses β -hydrogen elimination reactions but increases the molecular weight of the produced polymer. Generally, metallocene complexes with hafnium as the central metal produce high molecular weight polyethylene, due to a more stable hafnium–carbon bond.¹¹⁵ Because of the kinetically labile zirconium–carbon bond, which facilitates the chain transfer via β -hydrogen elimination, metallocene and half-sandwich complexes of zirconium produce polyolefins with lower molecular weights (Figure 20).

IV.4. Metallocene Complexes that Produce Low Molecular Weight Polyethylene

In nearly all cases, low molecular weight polyethylene is produced by bridged metallocene complexes of zirconium generating an open bite angle at the

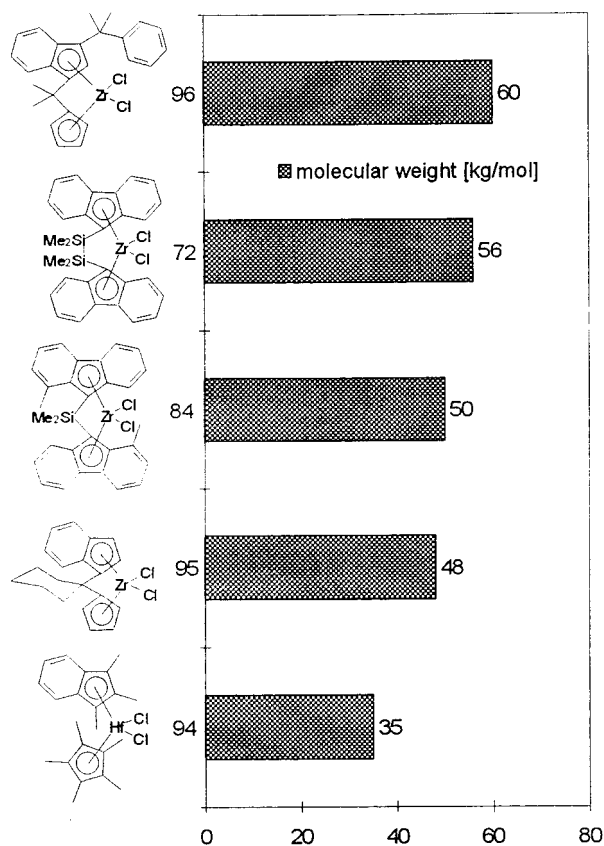


Figure 21. Polymerization conditions: $T_p = 60^\circ\text{C}$ (94–96, 72), 30°C (84); MAO, Al/Zr = 20000 (72), 8000 (84), 3000 (95, 96), 1000 (94); solvent *n*-pentane; 10.0 bar ethylene pressure.

active center that obviously is ideal for a premature chain-transfer step (Figure 21).

V. Acknowledgments

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