



# **Metallocene-Catalysed Polymerisation**

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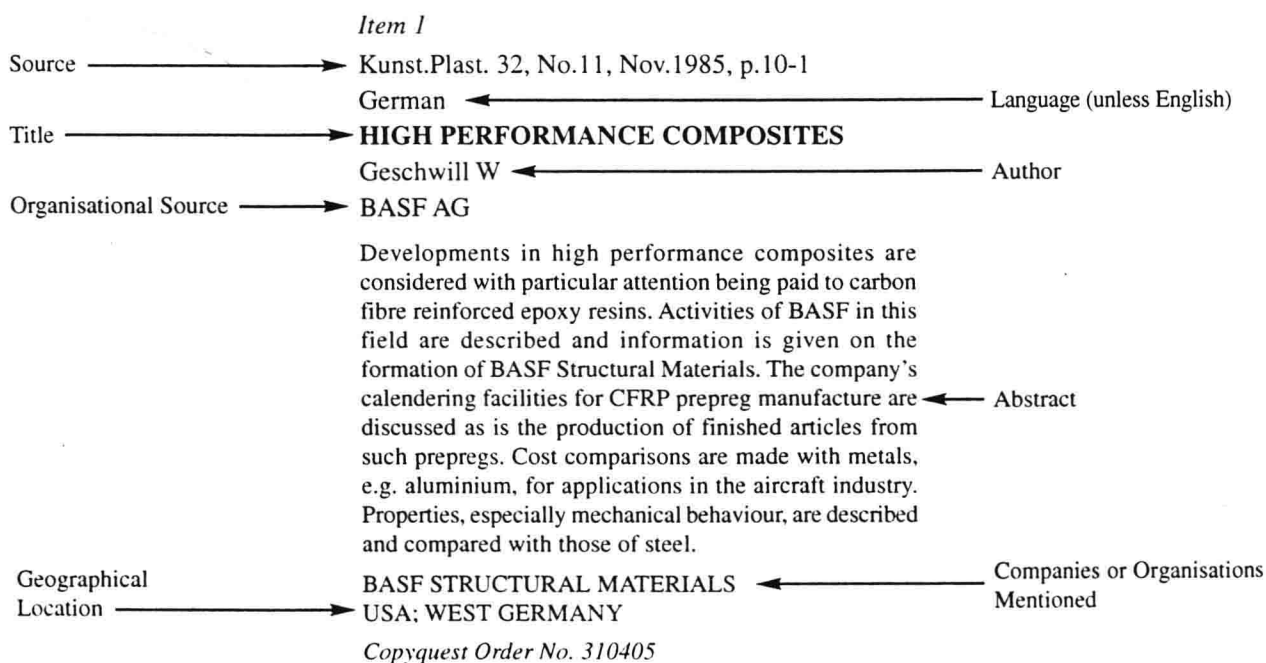
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## 1 SUMMARY

Metallocene-catalysed polymerisation of olefins, diolefins, styrene, and selected polar vinyl monomers is an important new technology that has started to make significant inroads into the plastics marketplace in recent years. Metallocenes have broadened our knowledge of the mechanism of Ziegler-Natta catalysis, of stereospecific polymerisation and of termination reactions. In contrast to heterogeneous Ziegler-Natta catalysts, the polymerisation takes place at a defined transition metal centre, which allows the control of the monomer insertion and other reaction steps more precisely. A great number of titanocenes, zirconocenes and hafnocenes with different symmetries have been synthesised, that give tailored polymers of totally different structures. Methylaluminoxane or other bulky cocatalysts are required for high activity. Single-site catalysts permit the user to control polymer tacticity, molecular weight and molecular weight distribution more efficiently. Beside the homopolymers of polyethylene and polypropylene, new kinds of copolymers and elastomers can be synthesised.

## 2 INTRODUCTION

The discovery of the polymerisation of ethene with  $\text{TiCl}_4/\text{AlEtCl}_2$  catalysts by Ziegler in 1953, shortly followed by that of the stereoselective polymerisation of propene by Natta, has developed a giant and important industry. Besides environmental applications and petroleum refining (denitrification in power plants, catalytic exhaust gas cleaning, catalytic oxidation of hydrocarbons, catalytic cracking of gas, naphtha, light oil), polymerisation is the greatest field for industrial catalysis.

Almost 40 million tons of polyethylene, polypropylene, copolymers and polydienes are produced worldwide - most with the help of the heterogeneous catalysts (112, 127). This accounts for 45 percent of the total production of plastics. It is estimated that in the year 2005 this figure will reach about 65 million tons and by the year 2020 about 150 million tons will be produced, i.e., about 55 percent of all plastics. This means that other plastics will be substituted by polyolefins in the future (129, 133, 156). What are the reasons for this? Polyolefins have an impact on everyday life, having an immense number of applications, ranging from the simple plastic bag made from polyethylene, to high modulus fibres, and the highly sophisticated capacitor film made of polypropylene (170). Use of metallocene catalysts

allows the structure of polymers to be tailored in a way which has not been possible before (75, 81, 86, 124, 224, 288, 342). Additionally, they allowed researchers to understand the mechanism and the stereochemistry of the polymerisation of olefins. Classical Ziegler catalysts are heterogeneous with the polymerisation taking place on dislocations and edges of the surface of  $\text{TiCl}_3$  or crystal mixtures of  $\text{MgCl}_2/\text{TiCl}_4$ . Consequently, there are many different types of active sites, and the resulting polymer has a typically broad molecular weight distribution. Cossee et al. (a.1) introduced the hypothesis that the insertion of propene takes place in a *cis* conformation at a titanium-carbon bond. Natta postulated that for stereospecific polymerisation, chiral centres are needed on the surface to produce isotactic polymers. These and other questions about the nature of the active sites increase the interest in investigations of the homogeneous metallocene catalysts (225).

### 2.1 History of Metallocene Polymerisation Catalysts

Metallocenes have been known for a long time. In 1952, Wilkinson and Fischer solved the structure of ferrocene. This new class of compounds, with a spatial arrangement reminiscent of a sandwich, gave organometallic chemistry greater versatility but failed to have an impact on industrial scale applications. Soon after the important discovery by Ziegler and Natta, metallocenes were used as transition metal compounds in combination with aluminiumalkyls, such as triethylaluminium and diethylaluminium chloride, for the polymerisation of olefins. The activities of these catalysts were poor and so the metallocenes were only used for scientific, mainly mechanistic studies, which were simpler with a hydrocarbon-soluble (homogeneous) system than a heterogeneous Ziegler system.

In comparison to the titanocenes, the zirconocenes show no polymerisation activity with aluminiumalkyls. An increase in the activity was made by addition of small amounts of water to a system of titanocenes and ethylaluminium chlorides.

However, this situation changed dramatically when, in 1975, water accidentally got into a test tube used for NMR measurements which contained biscyclopentadienyltitaniumdimethyl, trimethylaluminium and ethene. Suddenly, the ethene began to polymerise quickly, in a system thought at that time to be inactive for olefin polymerisation.

The intensive search for the active cocatalyst responsible for this activation led, in 1977, to the

isolation of methylaluminoxane (MAO), a component in which aluminium and oxygen atoms are alternately positioned and free valences are saturated by methyl groups (a.2). The structure of MAO is described further in Section 2.3.1.

If metallocenes, especially zirconocenes, are combined with MAO, the resulting catalyst can polymerise olefins 10-100 times faster than those used in the most active Ziegler-Natta systems (342).

In 1982, Hans Brintzinger at the University of Konstanz synthesised a chiral ansa-bisindenyl titanocene with  $C_2$ -symmetry (a.3). (Ansa metallocenes are more rigid because the cyclopentadienyl rings in the structure are tied together with a two carbon handle.) This compound was used, in 1984 by John Ewen (then at Exxon), in combination with MAO to first demonstrate the synthesis of isotactic structures by propene polymerisation (a.4). Around the same time it was shown that the use of a chiral zirconocene leads to highly isotactic polypropylene.

Subsequently, Ewen and Razavi (369, a.5) produced another ansa zirconium metallocene with  $C_s$ -symmetry by cyclopentadienyl and fluorenyl ligands and used it to produce highly syndiotactic polypropylene. At the same time, Ishihara demonstrated that half-sandwich titanocenes were able to catalyse the production of syndiotactic polystyrene (398).

In 1990, James Stevens at Dow (a.6) made the remarkable discovery that titanium cyclopentadienyl amido compounds (constrained geometry catalysts) are very useful for the copolymerisation of ethene and longer chain  $\alpha$ -olefins.

## 2.2 New Possibilities

With the aid of metallocenes, plastics could be made for the first time with a property profile that is precisely controllable and within wide limits (182, 237, 254). This kind of precise control of properties such as temperature resistance, hardness, impact strength and transparency had not been possible before, because conventional Ziegler-Natta catalysts are generally solids on whose surface relatively non-uniform catalytic action takes place; this results in a corresponding non-uniformly composed polymer (163). As the catalyst itself is insoluble, its active sites are not accessible for analytical purposes. Therefore, it cannot be specifically improved on a rational basis. In contrast, with metallocene catalysts the polymer building blocks can be linearly joined together at a single site. Propene and

long-chain olefins can be built up stereoregularly, with the building blocks in the chain having a defined constantly repetitive configuration. This configuration has considerable influence on the service properties of the material. There is a variety of materials which can be very easily produced by metallocene catalysts (154, 231, 232, 275, 303). These include:

- polyethylene with a narrow molecular weight distribution, weight-average molecular mass ( $M_w$ )/number-average molecular mass ( $M_n$ ) = 2,
- long chain branched polyethylene,
- polypropylene (atactic, isotactic, isoblock, stereoblock, syndiotactic) with low amounts of oligomers,
- copolymers of ethylene with a high proportion (5-30 %) of a longer chain  $\alpha$ -olefins, such as 1-hexene, 1-octene,
- elastomers made of ethylene, propylene and dienes (EPDM),
- syndiotactic polystyrene with a melting point of 276 °C,
- mono- and copolymers of cycloolefins,
- 1,5 hexadiene copolymers and
- ethene and propene polymers in the presence of fillers, filled polyolefins, blends.

All these polymers have unique properties which may not be achieved with classical Ziegler-Natta and Phillips catalysts (155).

## 2.3 Activation of the Catalyst

A key to the high polymerisation activity of single-site catalysts are the cocatalysts. MAO is used most and is synthesised by controlled hydrolysis of trimethyl aluminium. Other bulky anionic complexes which show a weak coordination, such as borates, play an increasing role, too. One function of the cocatalysts is to form a cationic metallocene and an anionic cocatalyst species. Another function of MAO is the alkylation of halogenated metallocene complexes. In the first step, the monomethyl compound is formed by transfer of a methyl from the MAO to the metallocene, within seconds, even at -60 °C. Excess MAO leads to the dialkylated species, as NMR measurements show. In

order for the active site to form, it is necessary for at least one alkyl group to be bonded to the metallocene.

Other alkylaluminoxanes, such as ethylaluminoxane (EAO) or isobutylaluminoxane (IBAO) were used as cocatalysts instead of methylaluminoxane. Both show a much lower polymerisation activity, similar to the use of simple trialkylaluminium.

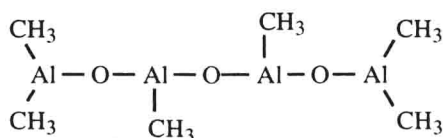
### 2.3.1 Methylaluminoxane

Alkylaluminoxanes may be prepared in a variety of ways. The preferred reaction of trimethylaluminium with water (ice) is a violent, highly exothermic reaction and is best carried out at low temperatures in an inert solvent. Instead of water, salt hydrolysis of  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  can be used. In both cases, the reaction is evidenced by the evolution of methane during the hydrolysis.



Unfortunately, this reaction is a gross simplification of the series of reaction steps that occurs during the hydrolysis reaction. The hydrolysis has been shown to proceed via the formation of an alkylaluminium water complex, which subsequently eliminates methane to form a dimethylaluminium hydroxide complex. This rapidly associates to give dimers or larger oligomers in solution. In the case of *t*-butylaluminoxane, some of the intermediate species have been isolated and structurally characterised.

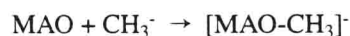
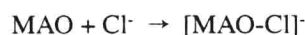
The structure of MAO is complex and has been investigated by cryoscopic measurements, by hydrolysis reactions, by infrared (IR), ultraviolet (UV), mass and nuclear magnetic resonance (NMR) spectroscopic measurements and by other methods (350). Various equilibria exist between the oligomers. The molecular weight, determined cryoscopically in benzene, lies between 1000 and 1500 g/mol. Since the work of Sinn (340) and Barron (341), more details about the structure of methylaluminoxane and *t*-butylaluminoxane have become known. Amongst the different oligomers,



units are important. These units can associate resulting in coordination of the unsaturated aluminium atoms.

There are tri- and tetra-coordinated aluminium atoms, of which the trivalent show extreme Lewis acidity. Four of the  $\text{Al}_4\text{O}_3(\text{CH}_3)_6$  units can form a cage structure resembling a half open dodecahedron ( $\text{Al}_{16}\text{O}_{12}(\text{CH}_3)_{24}$ ).

This cage is complexed with differing amounts of trimethylaluminium. The MAO complex can seize a methyl anion, a chlorine anion or another O-R anion from the metallocene, forming an MAO-anion which can distribute the electron over the whole cage, thus stabilising the charged system.

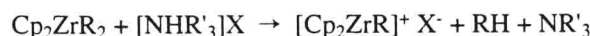


There is great evidence that the cationic  $\text{L}_2\text{M}(\text{CH}_3)^+$  is the active centre in olefin polymerisation (where M is a transition metal of the active species such as Ti, Zr or Hf, and L is a bonded ligand such as cyclopentadienyl, indenyl or fluorenyl).

The appearance of cationic metallocene complexes  $\text{L}_2\text{MCH}_3^+$ , especially  $\text{Cp}_2\text{ZrCH}_3^+$  (where Cp is cyclopentadienyl), in the presence of MAO-solution was confirmed by  $^{13}\text{C}$ -NMR,  $^{91}\text{Zr}$ -NMR and X-ray measurements. The cation is stabilised by weak coordination to Al-O units or bridging  $\text{CH}_3$  or Cl ligands.

### 2.3.2 Perfluorophenylborane and Perfluorophenylborate

Further evidence for the existence of cationic centres is given by the activation of metallocene catalysts by anionic counterions such as tetraphenyl borate ( $(\text{C}_6\text{H}_5)_4\text{B}^-$ ), carborane ( $\text{C}_2\text{B}_9\text{H}_{12}^-$ ) or fluorinated borate. The use of  $(\text{C}_6\text{H}_5)_4\text{B}^-$  as counter ion by Hlatky and Turner (a.7) and other research groups (245) led to highly active metallocene catalysts. These are formed by the reaction of a dealkylated zirconocene with dimethylaniliniumtetrakis(pentafluorophenyl)borate.



Cationic metallocene complexes can also be formed by reaction with perfluorinated triphenylborane or trityltetrakis(pentafluorophenyl)borate.

Early studies had shown that even donor-stabilised metal alkyl cations are very potent electrophiles which do not tolerate conventional anions such as  $\text{BF}_4^-$  and  $\text{PF}_6^-$  but

which will form insoluble salts with  $\text{B}(\text{C}_6\text{H}_5)_4^-$ . These studies showed that the formation of a cationic catalyst leads to a complex equilibrium of various adducts of the highly electron-deficient  $[\text{Cp}_2\text{ZrR}]^+$  cation. The amine liberated during the protolysis step, the counterion and the solvent are capable of binding to the cationic metallocene. Under polymerisation conditions this means that all these adducts are in competition with the polymerisation active species (244).

X-ray analysis of solid compounds such as  $[[(\text{CH}_3)_2\text{C}_5\text{H}_3]_2\text{ZrCH}_3]^+ + [\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$  shows that a coordination bond still partly exists between the zirconocene and the borate. The olefin is bonded through the  $\pi$ -electrons into this compound first and then inserted into the zirconium-methyl bond.

The active ion pairs are presumed to be either associated, with a very weak  $\text{Zr}\dots\text{F}-\text{C}$  coordination for  $(\text{C}_6\text{F}_5)_4\text{B}^-$  but a stronger  $\text{Zr}\dots\text{CH}_3-\text{B}$  bond for  $(\text{C}_6\text{F}_5)_3\text{B}(\text{CH}_3)^-$ , or to be completely dissociated. The catalysts with  $\text{MAO}^-$  ( $\text{MAO}-\text{Cl}^-$ ,  $\text{MAO}-\text{CH}_3^-$ ) and  $(\text{C}_6\text{F}_5)_4\text{B}^-$  are generally more active than those paired with  $(\text{C}_6\text{F}_5)_3\text{B}(\text{CH}_3)^-$ .

A great advantage is that the required ratio of borate to metallocene is about 1:1 and not 5000:1, as in the case of MAO for homogeneous systems (335). On the other hand, the borate system is very sensitive to contamination and decomposition and must be stabilised by addition of aluminiumalkyls such as triisobutylaluminium (TIBA); the necessary ratio of TIBA to zirconocene is in the range of 100:1 to 500:1.

### 2.3.3 Role of the Cocatalyst

The cocatalyst has different functions (128). The primary role of methylaluminoxane, as a cocatalyst for olefin polymerisation with metallocenes, is alkylation of the transition metal and the production of alkyl complexes of the type  $\text{Cp}_2\text{MR}^+$  as the catalytically active species. Indirect evidence that MAO generates metallocene cations has been furnished by the above described perfluorophenylborate and by model systems. The direct elucidation of the structure and the function of MAO is hindered by the presence of multiple equilibria, such as produced by disproportionation reactions between oligomeric MAO chains. Moreover, some unreacted trimethylaluminium always remains bound to the MAO and greatly influences the catalyst performance. The reactions between MAO and zirconocenes are summarised in **Figure 1**.

Even at  $-60^\circ\text{C}$  the metallocene and MAO form a complex, as shown by IR measurements of a new

absorption maximum (339). Following complexation, rapid alkylation and dissociation into an ion pair occur. An equilibrium exists between the ion pair of the cationic metallocene and the anionic MAO and the resulting complexes. Both systems show polymerisation activity, but the cationic complex is significantly more active. The polymers produced have different molecular weights and show a bimodal molecular weight distribution (200).

An important side reaction is  $\alpha$ -hydrogen transfer which causes the production of methane. Condensation of the metallocene and MAO takes place forming  $\text{Zr}-\text{CH}_2-\text{Al}-$  or  $\text{Zr}-\text{CH}_2-\text{Zr}-$  structures. These compounds are inactive and are one reason for the deactivation of metallocene catalysts (a.8).

The condensation rate depends on the structure of the zirconocene, the temperature, the Al/Zr ratio and the concentration. The methane production is much faster with MAO than with the less Lewis-acidic trimethylaluminium. More than 10 moles of methane are eliminated per mole of zirconium in 2 hours when the aluminium/zirconium ratio is high. The picture is complicated by self-condensation of MAO. The high amount of methane production and the creation of  $\text{Zr}-\text{CH}_2-\text{Al}-$  structures means that the catalyst becomes inactive after some minutes. As the metallocene catalyst is active for hours or even days, there has to be a reactivation step.

It was observed by dynamic  $^1\text{H}$ -NMR measurements that inactive  $\text{Zr}-\text{CH}_2-\text{Al}-$  structures could be activated by an excess of MAO, forming  $\text{L}_2\text{ZrCH}_3\text{Cl}$  and  $\text{Al}-\text{CH}_2-\text{Al}$  structures. Using  $\text{Cp}_2\text{ZrCl}_2$ , the cyclopentadienyl rings give sharp signals, which have a different chemical shift for all intermediates. After 20 to 120 minutes, an equilibrium exists between deactivation and reactivation.

In **Table 1** polymerisation activity is correlated with the evolution of methane as a function of reaction time. Around 15 minutes after mixing, the metallocene/MAO catalyst reaches its maximum activity; the production of methane is low. Under methane production deactivation occurs (see **Figure 1**) and the polymerisation activity decreases. After 2 hours at  $10^\circ\text{C}$  equilibrium is reached between deactivation and reactivation as evidenced by a constant polymerisation rate. This activity is then nearly constant over 17 hours. Therefore, another important function of MAO is the reactivation of inactive complexes formed by hydrogen transfer reaction.

With perfluorophenylborate, the side reactions are not known in detail. Unfluorinated borates show a





**Table 1. Polymerisation of propene with  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  after various prereaction times**

Prereaction time (h)	Yield (mol $\text{CH}_4$ (mol Zr) $^{-1}$ )	Rate of polymerisation (mol propene (mol Zr) $^{-1}$ s $^{-1}$ )
0.29	0.1	20.0
0.7	0.5	8.2
2.5	1.0	3.7
10.0	1.8	3.1
19.0	2.2	2.1

Polymerisation conditions: 105 ml toluene, 37 ml propene (3 bars), temperature = 10 °C,  $[\text{Zr}] = 10^{-5}$  mol l $^{-1}$ , reaction time = 20 h, MAO =  $3.6 \times 10^{-2}$  mol/Al l $^{-1}$ . Prereaction: 50 ml toluene, 10 °C,  $[\text{Zr}] = 4 \times 10^{-3}$  mol l $^{-1}$ , MAO = 1.68 mol/Al l $^{-1}$

fast interaction with the metallocenes. A substantial reduction in cation-anion interaction was achieved using perfluorotetraphenylborate  $\text{B}(\text{C}_6\text{F}_5)_4^-$  as the counteranion (a.9). This borate is considerably less basic and less prone to phenyl transfer reactions than  $\text{BPh}_4^-$  and can be used to high polymerisation temperatures. As no alkylation is possible, the metallocenes must be dialkylated from the beginning or an alkylaluminium has to be added. Using  $\text{B}(\text{C}_6\text{F}_5)_3$  with dimethyl zirconocenes offers the advantage that the product is stabilised by methyl coordination and is less polar and significantly more soluble in toluene. In contrast to the methyl complexes, the reaction of zirconocene dibenzyls with  $\text{B}(\text{C}_6\text{F}_5)_3$  gives only ionic products.

### 3 METALLOCENES FOR ETHENE POLYMERISATION

#### 3.1 Homopolymerisation

Using bis(cyclopentadienyl)zirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) and MAO, up to 40,000,000 g polyethene/g Zr·h $^{-1}$  are obtained.

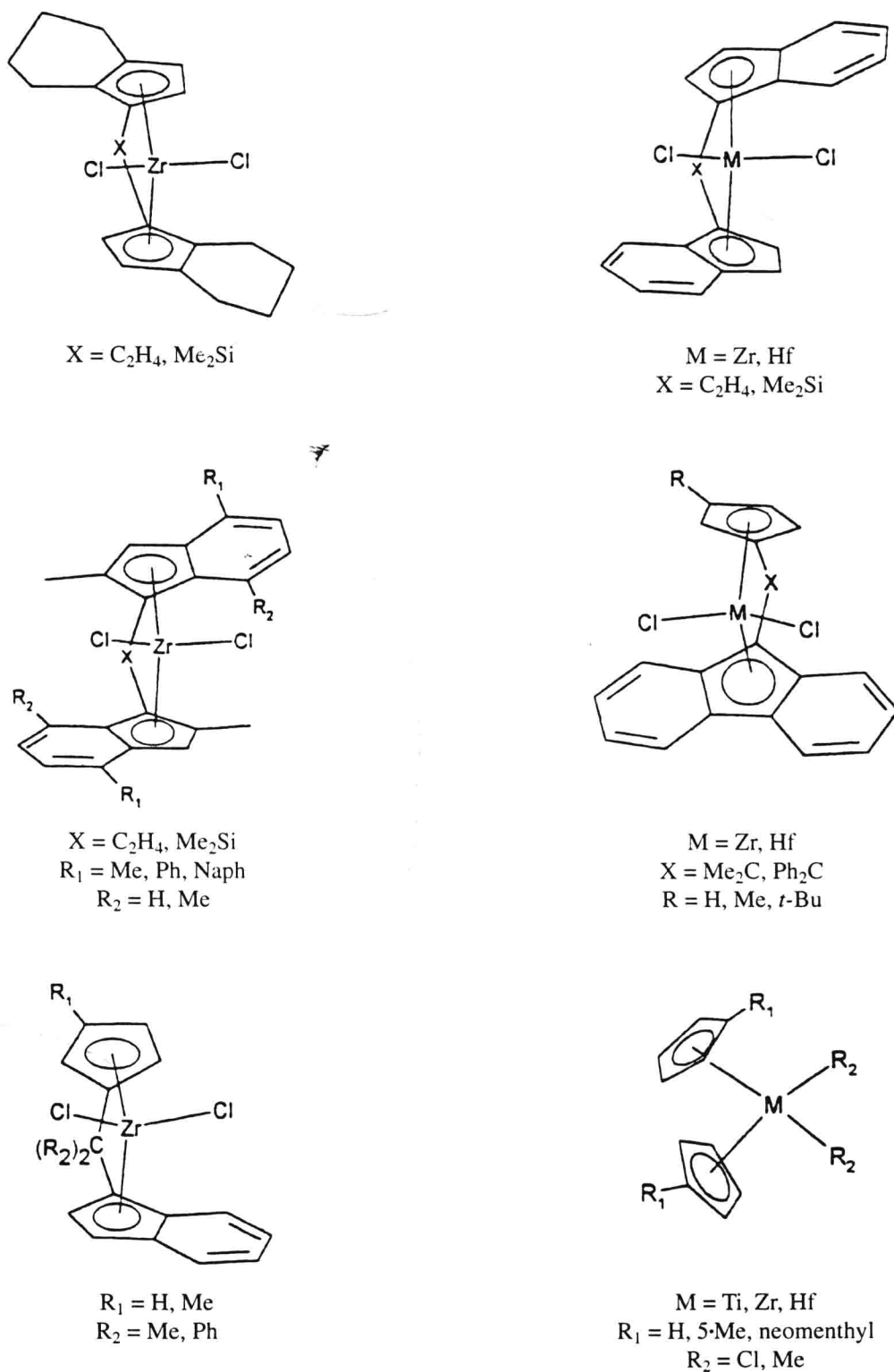
Each zirconium atom forms an active complex, as shown by Tait et al. in Manchester (396) and Chien et al. in Massachusetts (395), and produces about 46,000 polymer chains per hour. The insertion time of one ethene unit is only  $3 \times 10^{-5}$  seconds. This time is similar to those observed for synthesising enzymes. The analogy can be seen in many other fields too (influence of substitution, regioselectivity, stereospecificity).

Unbridged, bridged, substituted and half-sandwich complexes have been used as metallocene catalysts for ethene polymerisation (261). Some of the classes of metallocene catalysts used for the polymerisation of ethene are shown in **Figure 2**. In order to compare the activity of the catalyst and molecular mass of the polymer, the polymerisations are carried out under the same conditions (30 °C, 2.5 bar ethene pressure, toluene as solvent).

The polymerisation behaviour of different metallocene aluminoxane catalysts is given in **Table 2**. Generally, zirconium catalysts are more active than the hafnium or titanium systems (321, 381). Partially substituted bisindenyl systems and bridged bisfluorenyl zirconocenes show very high activities, exceeding those of the less sterically hindered  $\text{Cp}_2\text{ZrCl}_2$ . Zirconocenes with bulky ligands, such as neomenthyl substituted derivatives, afford significantly lower productivity. This indicates that electron-donating groups can enhance productivity, whereas steric crowding lowers it. Among the different aluminoxane cocatalysts, methylaluminoxane is much more effective than ethyl- or isobutylaluminoxane. The catalyst shows a long-lasting activity, even after a polymerisation time of more than 100 hours. The maximum activity is reached after 5 to 10 minutes. This time seems to be needed for the active site to form.

Different zirconocenes produce high density polyethylene (HDPE) with very different molecular weights (304, 381). In ethene-based polymers, increasing the size of the Cp substituent (for example, methyl, ethyl, butyl, octyl) increases the molecular weight of the copolymer, while there is only a minor dependence on the cocatalyst. For example,





**Figure 2**

Structures of selected metallocenes used for the polymerisation of olefins