CHAPTER II
LITERATURE SURVEY

Olefins are traditionally polymerized using Ziegler-Natta or Phillips type catalysts, but more recently, worldwide efforts have been put into the development of metallocene type catalysts (Parshall and Ittel, 1992). Polyolefins are very important commodity polymers. Polyethylene and polypropylene are today the major tonnage plastic materials worldwide. Metallocene catalysts with aluminoxane and other cocatalysts are able to produce polyolefins at a very high productivity with a degree of microstructural control not possible to achieve using conventional Ziegler-Natta catalysts (Hamielec and Soares, 1996).

Transition metal catalyzed olefin polymerization started with the work done in the United States and Europe in the early 1950s. Karl Ziegler found that transition metal salts in combination with triethylaluminum (TEA) produced a white solid when reacted with ethylene.

2.1 Ziegler–Natta Catalysts

Ziegler-Natta catalsyts are formed by a transition metal salt of metals of groups IV-VIII and a metal alkyl of a base metal of groups I – III (known as cocatalyst or activator). However, not all combinations are equally efficient for all monomers. From the industrial point of view, most heterogeneous catalysts are based on titanium salts and aluminum alkyls (Boor, 1979).

Most types of heterogeneous Ziegler-Natta catalysts have a common characteristic: they yield polymers with broad molecular weight distribution (MWD) and, in the case of copolymerization, broad chemical

composition distribution (CCD). There is now a general agreement that heterogeneous Ziegler-Natta catalysts possess more than one type of active sites, each one with distinct ratio of chain transfer to propagation rate, comonomer reactivity ratio, and stereoselectivity. Each type makes polymer chains that have different average chain lengths, comonomer compositions, comonomer sequence lengths, and in the case of asymmetrical monomers, different degrees of stereoregularity. Consequently, heterogeneous Ziegler-Natta catalysts produce a mixture, at the molecular level, of polymer chains having dissimilar average properties as reflected in broad MWD and CCD. Additionally, intraparticle heat- and mass-transfer resistance during the polymerization may somewhat broaden these distributions even further. Table 2.1 lists the chronology of development in Ziegler-Natta catalysts.

On the other hand, polyolefins made with several metallocene systems, including most soluble Ziegler-Natta catalysts, have narrow MWD, and copolymers also have narrow CCD (Dube *et al.*, 1997).

2.2 Homogeneous Metallocene Catalysts

2.2.1 Introduction

Metallocene single-site catalyst technology is a major advance in polyolefin formation. This is because single-site catalyst (SSC) technology allows unprecedented control over reactivity. The technology can enhance existing products and create polymers with distinct properties and process advantages. Uniformity of the active site in these systems leads to greater uniformity of the polymer microstructure and molecular weight distribution. Additionally, comonomer incorporation with metallocene catalysts is generally uniform throughout the spectrum of molecular weights. Metallocene-based products, both conventional and new polymers, are appearing on the market more and more frequently.

Table 2.1 Chronology of development in Ziegler-Natta catalysts (Reddy and Sivaran 1995).

Year	Catalyst system	Polymer	Activity (kg-Polymer/ g-metal.h)	Tacticity (%)
1953–1955	$TiCl_4$-Et_3Al	Polyethylene	10–15	–
		Polypropylene	5–10	50–60
	$TiCl_3$-Et_3Al	Polyethylene	5–10	–
		Polypropylene	1–3	60–80
1955–1960	$TiCl_3$ Electron Donors-Et_3Al	Polyethylene	–	–
		Polypropylene	1–10	90–95
1970–Present	Supported $MgCl_2$ $TiCl_2$-Et_3Al	Polyethylene	500–1000	–
		Polypropylene	500–1000	50–70
	Supported $MgCl_2$.Electron Donor.$TiCl_4$-Et_3Al	Polyethylene	500–1000	–
		Polypropylene	300–500	90–99
1980–Present	Homogeneous Metallocene-Methylaluminoxane	Polyethylene	400–500	–
1985–Present	Stereorigid Metallocene-Methylaluminoxane	Polypropylene	150–170	96–98
	Homogeneous Aluminum Free Metallocene catalysts	Polypropylene	0–1	97–98
	Supported metallocene catalysts/AlR_3 or MAO	Polypropylene	10–20	80–90
1986–Present	$Ti(OR)_4$-MAO	Syndiospecific-	0.4–0.5	80–96
	$CpTi(OR)_3$–MAO	polystyrene	3300	82
	$Mg(OH)_2/Ti(OBu)_4$–MAO		0.3	100
1988–Present	Cp_2ZrCl_2–MAO	Ethylene–Porpylene	50–100	Aspecific
	$Et[IndH_4]_2ZrCl_2$–MAO	co-polymer	5–15	Isospecific
	i-$Pr(Cp)(Flu)ZrCl_2$–MAO			Syndiospecific
	Cp_2ZrCl_2–MAO	Ethylene–Hexene co-	–	Aspecific
	$Et[IndH_4]_2ZrCl_2$–MAO	polymer		Isospecific
	i-$Pr(Cp)(Flu)ZrCl_2$–MAO			Syndiospecific
1988–Present	$Et[Ind]_2ZrCl_2$–MAO	Ethylene–cyclic olefin co-polymers	0.02–0.14	–

6

Medium MW/Medium branching   Low MW/High branching

b a
c   ←— catalyst support   Multi–Site

High MW/Low branching
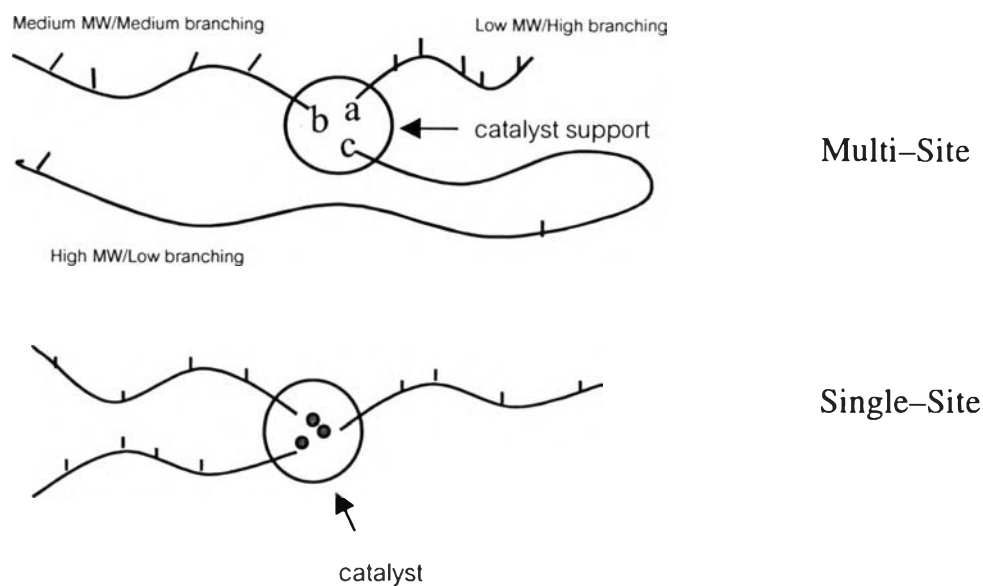
Single–Site

catalyst

Figure 2.1 Single-site versus multisite catalysts (Huang and Tian, 1996).

Metallocene catalysts have been used to produce polyolefins commercially since 1991. The commercial interest centers on their use in making polyethylene (PE) and polypropylene (PP). PE is the world's largest volume bulk plastic with annual consumption approaching 35 Mt. PP is the third-ranked bulk plastic (after PVC) with annual consumption of about 17 Mt. These two polyolefins alone account for 35% of all thermoplastics and elastomers (Sinclair and Wilson, 1994). Table 2.2 lists the monomers that can be polymerized with metallocene catalysts. In addition, metallocenes can readily polymerize bulky monomers such as styrene and norbornene to make novel polymers with physical properties such as nylon, polycarbonates and polyesters. Any technology with such broad applicability is bound to be of great interest to the plastics industry (Kaminsky, 1996).

2.2.2 History

Metallocenes are relatively old organometallic complexes that were discovered as early as 1951. The first compound discovered was ferrocene, a simple complex consisting of an iron center and two cyclopentadienyl (Cp)

rings surrounding the metal. The term metallocene was used to describe any complex with a metal center and Cp ligands surrounding it. Presently, the term

Table 2.2. Monomers that can be polymerized with metallocene catalysts (Sinclair and Wison, 1994)*.

Acetylene

Olefins and diolefins

Ethylene	Octene-1	3-Methyl butene-1
Propylene	Hexadecene-1	4-Methyl pentene-1
Butene-1	Octadecene-1	4-Methyl hexene-1
Pentene-1	1,3-Butadiene	1,5-Hexadiene
Hexene-1	Dimethano-	1,6-Octadiene
1,4-Hexadiene	octahydronaphthalene (DMON)	1,4-Dodecadiene

Aromatics

Styrene	*p-tert*-Butylstyrene	Indene
o-Methylstyrene	*m*-Chlorostyrene	4-Vinylbiphenyl
m-Methylstyrene	*p*-Chlorostyrene	Acenaphtahlene
p-Methylstyrene	*p*-Fluorostyrene	Vinylfluorene
Vinylanthracene	Vinylpyrene	Vinylchrysene

Cyclic olefins and diolefins

Cyclopentene	*tert*-Ethylidene-2-	4-Vinylbenzocyclobutane
3-Vinylcyclohexene	norbornene	Tetracyclododecene
Dicyclopentadiene	7-Octenyl-9-	(TCD-3)
5-Vinyl-2-norbornene	borabicyclo-(3,3)nonane	

Esters, silanes, boranes, others

Methylmethacrylate	Phenyl silane	Acrylic acid
Ethylacrylate	Trimethylallyl silane	2-Ethylhexylacrylate
Vinyl silane	Acrylonitrile	*N*-Phenylmaleimide
Methacrylic acid	maleimide	Methacrylonitrile

Others claimed but not illustrated

Vinyl chloride	Isobutylene	Tetrafluoroethylene
Vinylidene chloride	Carbon monoxide	Norbornene

*Demonstrated in patent examples

is used to describe a wide variety of organometallic complexes including those with modified structures such as substituted Cp rings and bridging atoms.

There are three general categories of cyclopentadienyl transition-metal complexes:

(a) symmetrical molecules with parallel cyclopentadienyl rings,

(b) bent metallocenes in which the number of ligands L can vary from one to three,

(c) complexes containing only one cyclopentadienyl ring in which the number of ligands L can vary from one to four.

Because of their characteristic structures, metallocenes have been called "sandwich compounds" or "half-sandwich compounds".

In 1957, Natta and Pino (1957) reported the polymerization of ethylene with the titanocene catalyst, Cp_2TiCl_2. This was accomplished with the cocatalyst, trimethylaluminm, although the activity of the metallocene was found to be very low and there was little promise for commercial use. In the mid 1970's, Walter Kaminsky (1983) was experimenting with a metallocene catalyst of the form Cp_2ZrCl_2 and the cocatalyst $Al(CH_3)_3$. Water was accidentally introduced into the system that led to high activity between the catalyst and ethylene monomer to form polymer. After further research, it was believed that the high activity was a result of the hydrolysis of the cocatalyst trimethyl aluminum to form methylaluminoxane or MAO.

2.3 Metallocene Catalyst Systems

Metallocene catalyst systems can be conveniently divided into two categories. In the first category, an aluminoxane, an alkylaluminum, or a combination of aluminoxane and alkylaluminum, are used to activate the metallocene catalyst. In general, these metallocenes have poor or no activity when used alone. In the second category, an ion exchange compound is combined with the metallocene catalyst, forming what is generally called a

cationic metallocene catalyst. It is now generally accepted that the catalytic active species for metallocene/aluminoxane/alkyaluminum systems is also cationic. Table 2.3 gives some examples of metallocenes.

Table 2.3 Representative examples of metallocenes (Gupta *et al.*, 1994).

[A] Nonstereorigid metallocenes:

    1) Cp_2MCl_2 (M = Ti, Zr, Hf)

    2) Cp_2ZrR_2 (R = Me, Ph, CH_2Ph, CH_2SiMe_3)

    3) $(Ind)_2ZrMe_2$

[B] Nonstereorigid ring-substituted metallocenes:

    1) $(Me_5C_5)_2MCl_2$ (M = Ti, Zr, Hf)

    2) $(Me_3SiCp)_2ZrCl_2$

[C] Stereorigid metallocenes:

    1) $Et(Ind)_2ZrCl_2$

    2) $Et(Ind)_2ZrMe_2$

    3) $Et(IndH_4)_2ZrCl_2$

[D] Cationic metallocenes:

    1) $Cp_2MR(L)^+[BPh_4]^-$ (M = Ti, Zr)

    2) $[Et(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$

    3) $[Cp_2ZrMe]^+[C_2B_9H_{11})_2M]^-$ (M = Co)

[E] Supported metallocenes

    1) Al_2O_3-$Et(IndH_4)_2ZrCl_2$

    2) $MgCl_2$•Cp_2ZrCl_2

    3) SiO_2•$Et(Ind)_2ZrCl_2$

2.3.1 Metallocene catalyst systems containing aluminoxane compounds

    In 1980 Kaminsky and coworkers used oligomeric methyl aluminoxane (MAO) with group 4B metallocene compounds to obtain

ethylene polymerization catalysts having extremely high activities. For instance, Cp_2TiCl_2/MAO has a polyethylene productivity of 9.3×10^6 g PE/ (mol-Ti.h.atm) at 20 °C; the productivity is 9×10^7 g PE/(mol-Zr.h.atm) at 70 °C with Cp_2ZrCl_2/MAO. However, these catalysts are non-stereospecific producing only atactic polypropylene because of the symmetrical feature of their active centers. Table 2.4 gives examples of metallocene/aluminoxane catalyst systems.

2.3.1.1 Structure and role of methylaluminoxanes (MAO)

MAO is the most important cocatalyst which activates the group 4B metallocenes in homogeneous Zeigler–Natta polymerization. MAO is an oligomer with a degree of oligomerization varying between 4–20. The repeat unit is $-[Al(CH_3)-O]-$ (Reddy and Sivaran, 1995). A higher degree oligomerization of MAO provides a beneficial effect to the catalyst activity. The type of aluminoxane has a marked influence on the efficiency of the metallocene/aluminoxane catalytic system. Methylaluminoxane (MAO) seems to be more effective as a cocatalyst than other aluminoxanes such as ethylaluminoxane (EAO) and isobutylaluminoxane (IBAO).

MAO is synthesized by controlled hydrolysis of trimethylaluminum (TMA). Simple synthetic routes to MAO are not available due to the high reactivity of TMA with water. Many inorganic hydrated compounds are used as a source of water for preparing MAO from TMA. Hydrating compounds such as $CuSO_4 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 6H_2O$ are employed. Reddy and Sivaran (1995) and Bliemeister et al. (1995) recently published an extensive review of techniques for the synthesis of methylaluminoxane.

The exact structure of aluminoxanes is still a matter of controversy. Several structures have been proposed for MAO: rings, clathrates and linear or branched chains. The structure of MAO may depend upon the synthesis conditions, isolation methods, solvent used, and so forth. Earlier research

suggested that MAO might exist in a linear and/or a cyclic form. However, based on ^{27}Al NMR spectroscopic studies, some reserchers recently indicated that there appears to be no logical structure for MAO with $n > 4$ in which all aluminum atoms *simultaneously* achieve a coordination number of 4.

Table 2.4 Metallocene catalyst systems[*](Gupta *et al.,* 1994).

| Catalyst	Cocatalyst	Remark
1. Chlorocyclopentadienyl derivative of titanium: e.g., Cp$_2$TiCl$_2$	Dialkylaluminum chloride	Active for ethylene but inactive for propylene polymerization
2. Metallocene catalyst systems containing aluminoxane compounds	Aluminoxane	
2.1 Nonstereorigid metallocenes, e.g., Cp$_2$MX$_2$	Aluminoxane	a) High activity for ethylene polymerization b) Active for propylene polymerization (atactic polymer)
2.2 Stereorigid metallocenes, e.g., Et(Ind)$_2$MCl$_2$	Aluminoxane	Active for regio- and stereospecific polymerization of propylene
2.3 Supported metallocene catalysts, e.g., SiO$_2$-Et(Ind)$_2$MCl$_2$	Aluminoxane/ alkylaluminum	Active for ethylene and propylene polymerization
3. Metallocene catalysts systems containing nonaluminoxane compounds 3.1 Ionic metallocenes, e.g., [Cp$_2$MR(L)]$^+$[BPh$_4$]$^-$	—	Active for ethylene and propylene polymerization

*M = Ti, Zr, Hf
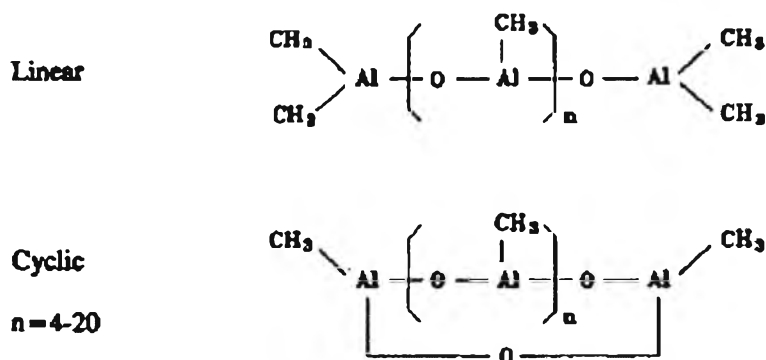
Figure 2.2 Linear and cyclic structures for methylaluminoxane.

A possible structure is shown in Figure 2.2 as proposed by Sugano (Huang and Rempel, 1995). The presence of some three-coordinate aluminum sites is to be expected and their Lewis acidity will be enhanced by the electronegative effect of adjacent oxygen atoms (see Figure 2.3 b).

2.3.2 Metallocene catalyst systems containing nonaluminoxane compounds

The need for very high aluminoxane to metallocene ratio, for example, Al/Zr = 50,000:1, for maximum activity highlights the need to develop aluminoxane-free cocatalyst systems. Active homogeneous catalysts can be obtained, in the absence of MAO, by allowing dialkyl metallocenes, such as $Cp_2Zr(CH_3)_2$, to react with strongly Brönsted acidic salts in a 1:1 mole ratio (Bochmann et al., 1990). The true active species produced in situ is basically a 14-electron cataionic complex, such as $[Cp_2ZrCH_3]^+$, which will be more or less affected by the counterion remaining in the system.

The active metallocene alkyl cation can be generated also by means of one of the following methods:

An ion pair $Cp_2^*Zr^+Me[B(C_6F_5)_4]^-$ (where Cp_2^* is some substituted Cp or indenyl ligand) is formed by reaction of $Cp_2^*ZrMe_2$ with dimethylanilinium tetrakis(perfluorophenyl)borate of by abstraction of CH_3^- from a (dimethyl) zirconocene complex by trithyl tetrakis(perfluorophenyl)borate (Equation 2.1 and 2.2) (Ewen and Elder, 1991).
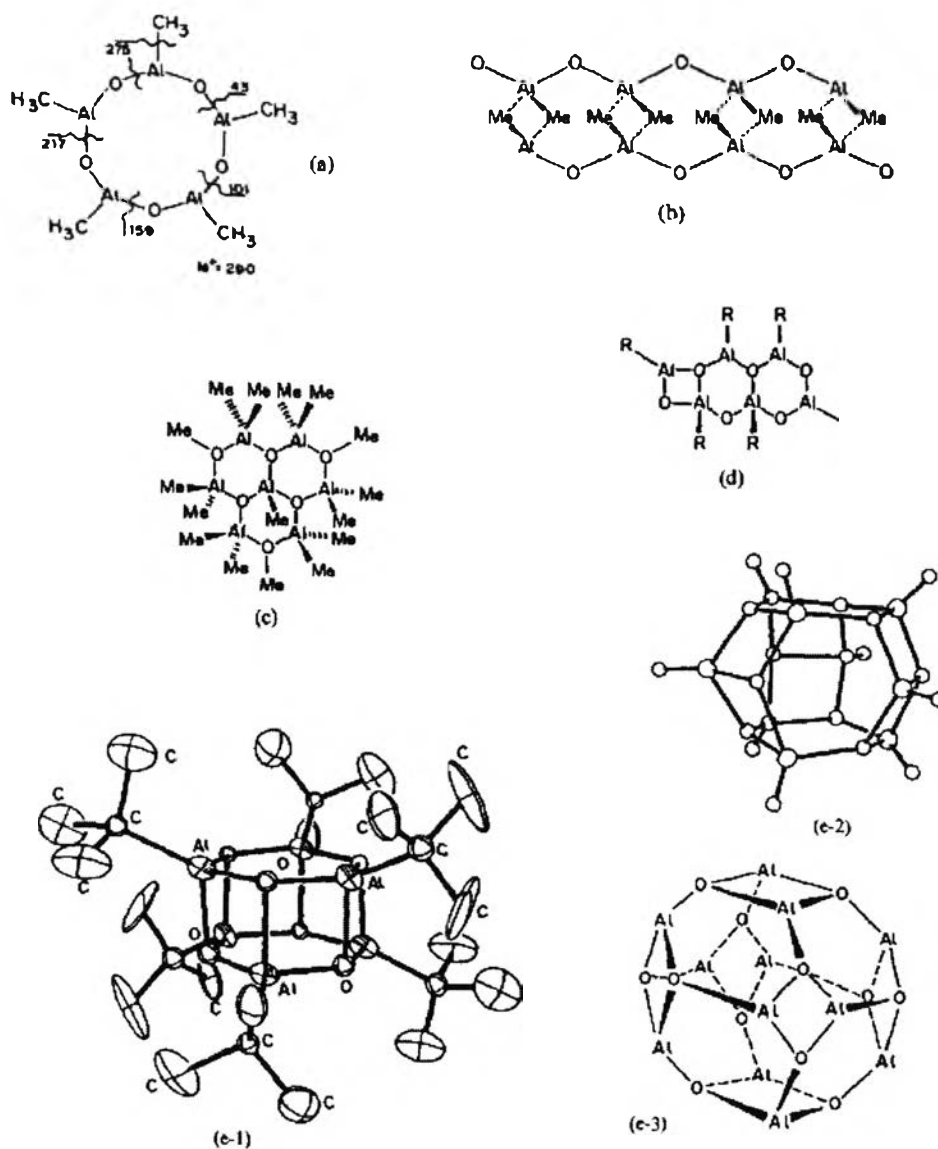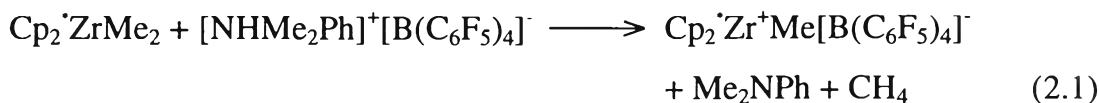
Figure 2.3 Different structures of aluminoxane. (a) Cyclic structure of MAO. (b) Linear tetracoordinated structure of MAO. (c) Structure of the $[Al_7O_6Me_{10}]^-$ anion. (d) Fused four six-membered ring structure. (e-1) Molecular structure of *tert*-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_6$, all the hydrogen atoms are omitted for clarity. (e-2) Molecular structure of *tert*-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_9$, methyl groups are omitted for clarity. (e-3) Plausible molecular structure of *tert*-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_{12}$, ^{t}Buthyl groups are omitted for clarity (Reddy, *et al.*, 1995).

$$Cp_2\text{*}ZrMe_2 + [NHMe_2Ph]^+[B(C_6F_5)_4]^- \longrightarrow Cp_2\text{*}Zr^+Me[B(C_6F_5)_4]^-$$
$$+ Me_2NPh + CH_4 \qquad (2.1)$$

$$Cp_2\text{*}MMe_2 + Ph_3C^+[B(C_6F_5)_4]^- \longrightarrow Cp_2\text{*}M^+Me[B(C_6F_5)_4]^- + Ph_3CMe \quad (2.2)$$

Cations obtained by abstraction of CH_3^- from a dimethylzirconocene complex by the powerful Lewis acid $B(C_6F_5)_3$ are likewise found to be highly active catalysts for α-olefin polymerization (Equation 2.3).

$$Cp_2MMe_2 + B(C_6F_5)_3 \longrightarrow Cp_2M^+Me[B(C_6F_5)_3Me]^- \qquad (2.3)$$

The coordination capability of the anion must be weak enough so as not to compete with the coordination of the monomer with the highly Lewis acidic metal center (Moore, 1996).

Cationic metallocene complexes, particularly those occur by in situ activation of a stable zirconocene precursor, yield catalysts with very high activities (Chien *et al.*, 1991). They are easily deactivated, however, probably by minute traces of impurities such as water and oxygen. Addition of $AlMe_3$ or $AlEt_3$ has been shown to stabilize these cationic metallocene catalysts by formation of AlR_3 adducts (Ewen and Elder, 1991).

2.4 Polymerization Mechanism

The Cossee-Arlman mechanism shown in Figure 2.4 is the most widely accepted mechamism for both Ziegler-Natta olefin polymerization and olefin polymerization by Kaminsky-type catalysts (Fan *et al.*, 1995).

The active species possesses a vacant coordination site, and for the group-4 transition metal (Ti, Zr, Hf) catalysts, this is the alkylated cationic metallocene. The first step of the process involves the complexation of olefin to form a π complex. In the second step, the olefin inserts into the metal–carbon bond through a four-membered cyclic transition state. The newly

formed species possesses a vacant coordination site where the M—C bond is formerly located.
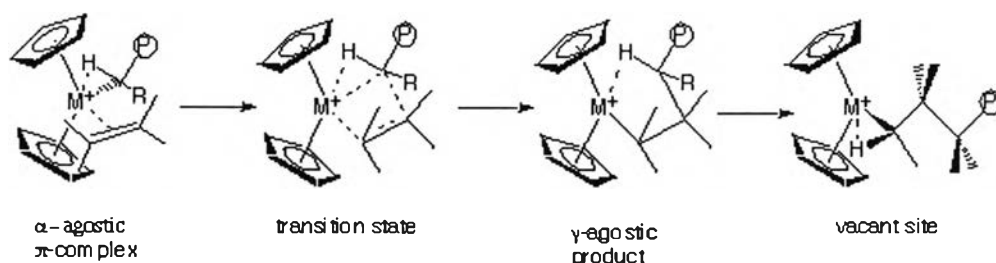

Figure 2.4 The Cossee–Arlman polymerization mechanism for metallocenes.

The Cossee–Arlman mechanism, although well accepted and understood in a conceptual sense, is not fully understood in a mechanistic sense. For example, the exact nature of the active species and the role of the cocatalyst and (or) counterion is a subject of debate. The current belief is that the active species is a cationic complex such as [Cp$_2$ZrR$^+$]. The role of the cocatalyst, usually MAO, is even less understood. It is thought that the cocatalyst may act only to generate the active species and remove impurities such as water from the system. On the other hand, it may play a more fundamental role such as assisting in the insertion of each monomer unit or reactivating dormant sites.

2.4.1 Catalyst forming reactions

MAO plays at least three roles in metallocene polymerizations: (a) it acts as an alkylating agent for the generation of a transition metal-alkyl molecule; (b) it acts as a Lewis acid for anion abstraction from the metal-alkyl molecule, generating an electrophilic species; and (c), where appropriate, it can act as a scavenger for the removal of impurities such as water.

When a toluene solution of Cp_2ZrCl_2 is treated with MAO, a fast ligand exchange takes place producing primarily $Cp_2ZrMeCl$, as is shown in Figure 2.5. The use of excess MAO produces Cp_2ZrMe_2.

However these systems only become catalytically active when Al:Zr ratio of greater than 200:1, or ever higher, is used. It is now recognized that either methyl or chloride abstraction by Al centers in the MAO takes place, as is shown in Figure 2.6. The active site is therefore regarded as a cationic 14-electron metallocene, which is loosely associated with the MAO anion.

Tait (1996), on the basis of active center studies, have postulated that in the Cp_2ZrCl_2–MAO catalyst system for ethylene polymerization, the propagation coeffecient of the uncharged $Cp_2ZrClMe$ (or Cp_2ZrClP) species is very much lower than that of the charged $[Cp_2ZrMe]^+$ or $[Cp_2ZrP]^+$ species. They have also maintained that the separated ion pair $[Cp_2ZrMe]^+$ and $[MAO (TMA)Cl]^-$ needs to be formed for high catalyst activity.

Metallocene catalyst systems require a large amount of methyl aluminoxane for achieving high productivity. The high cost of the cocatalyst has stimulated the search for new families of metallocene which can perform in the absence of aluminoxane.

2.4.2 Catalyst deactivation reactions

Metallocene dihalide–MAO catalysts show a more or less rapid exponential decay in the initial phase of polymerization before stabilizing at a lower level. With cationic metal alkyl catalysts, the initial activities are usually very high with an even more rapid decay. Catalyst deactivation is clearly an important consideration for any commercial use of these systems. However, there is so far very little information about possible deactivation pathways.

In early work Kaminsky and coworker (Kaminsky, 1996) succeeded in isolating a number of ethylene-bridged complexes from the reaction of
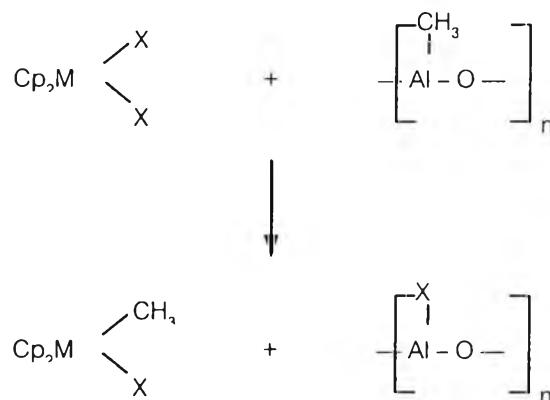
$$Cp_2M \begin{smallmatrix} \diagup X \\ \diagdown X \end{smallmatrix} \quad + \quad \left[\begin{smallmatrix} CH_3 \\ | \\ Al-O- \end{smallmatrix} \right]_n$$

$$Cp_2M \begin{smallmatrix} \diagup CH_3 \\ \diagdown X \end{smallmatrix} \quad + \quad \left[\begin{smallmatrix} X \\ | \\ Al-O- \end{smallmatrix} \right]_n \quad \cdot$$

Figure 2.5 Reaction of active species on interaction of a metallocene and excess MAO.

$$Cp_2M \begin{smallmatrix} \diagup CH_3 \\ \diagdown X \end{smallmatrix} \quad + \quad \left[\begin{smallmatrix} X \\ | \\ Al-O- \end{smallmatrix} \right]_n$$

$$Cp_2M \begin{smallmatrix} \diagup CH_3 \\ \end{smallmatrix} \quad + \quad \left[\begin{smallmatrix} X \quad X \\ | \diagup \\ Al-O- \end{smallmatrix} \right]_n^{(-)}$$
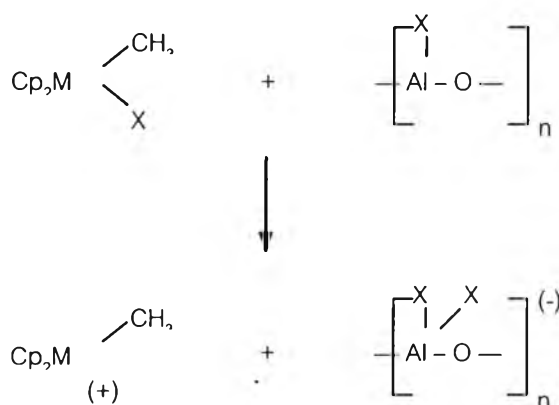$$(+)$$

Figure 2.6 Formation of active species on interaction of a metallocene and excess MAO.

[Cp$_2$ZrEt(Cl)] with AlEt$_3$ which were thought to be side products as shown in Figure 2.7 (a) and 2.7 (b).

Fischer and Mülhaupt (1991) determined the kinetics of catalyst deactivation for the atactic polymerization of propylene with Cp$_2$ZrCl$_2$–MAO catalysts. A reversible and an irreversible deactivation step could be distinguished, both second order in [Zr]. Although it is not possible to derive

firm conclusions about the nature of the deactivated species from such measurements, it is tempting to think that the reversible deactivation step consists of the formation of alkyl-bridged dinuclear zirconium complexes shown in Figure 2.7 (c).

Other potential deactivation pathways are the formation of dinuclear species by α- or β-CH activation. The chemistry of cationic group 4 alkyls provides examples of both. The fulvalene complex (Figure 2.7 (c)) reacts with CPh_3^+ or $B(C_6F_5)_3$ even at -60 °C with immediate elimination of methane to give a relatively inactive μ-CH_2 complex (Figure 2.7 (e)) and the hafnium ethyl complex (Figure 2.7 (f)) decomposes slowly with elimination of ethylene to give Figure 2.7 (g), a compound reminiscent of Figure 2.7 (b). The neutral dicarbollide complex [{$ZrCp^*(C_2B_9H_{11})Me$}$_n$] also decomposes via α-H elimination to a stable μ-CH_2 product (Figure 2.7 (d)), albeit at a much higher temperature of 45 °C for 2 h.

Cationic complexes containing $[B(C_6F_5)_4]^-$ and related counteranions may be expected to be prone to deactivation by aryl or fluoride transfer, although there is at present no evidence for this under catalytic conditions. Such reactions do, however, occur slowly at room temperature and above. For example, the reaction of Figure 2.7 (h) with $B(C_6F_5)_3$ in benzene over 24 h gives Figure 2.7 (i) and similarly Figure 2.7 (j) has been found to slowly form the fluoride complex, $[(ZrCp^*_2Me)_2(\mu\text{-}F)][MeB(C_6F_5)_3]$.

2.5 Tris(pentafluorophenyl) borane, $B(C_6F_5)_3$

2.5.1 Properties

Tris(pentafluorophenyl) borane was originally prepared by treating pentafluorophenyllithium with BCl_3 at -78 °C. A safter alternaive, especially for large scale synthesis, is to employ the Grignard reagent, pentafluorophenylmagnesium bromide, and a boron trihalide, since the lithium
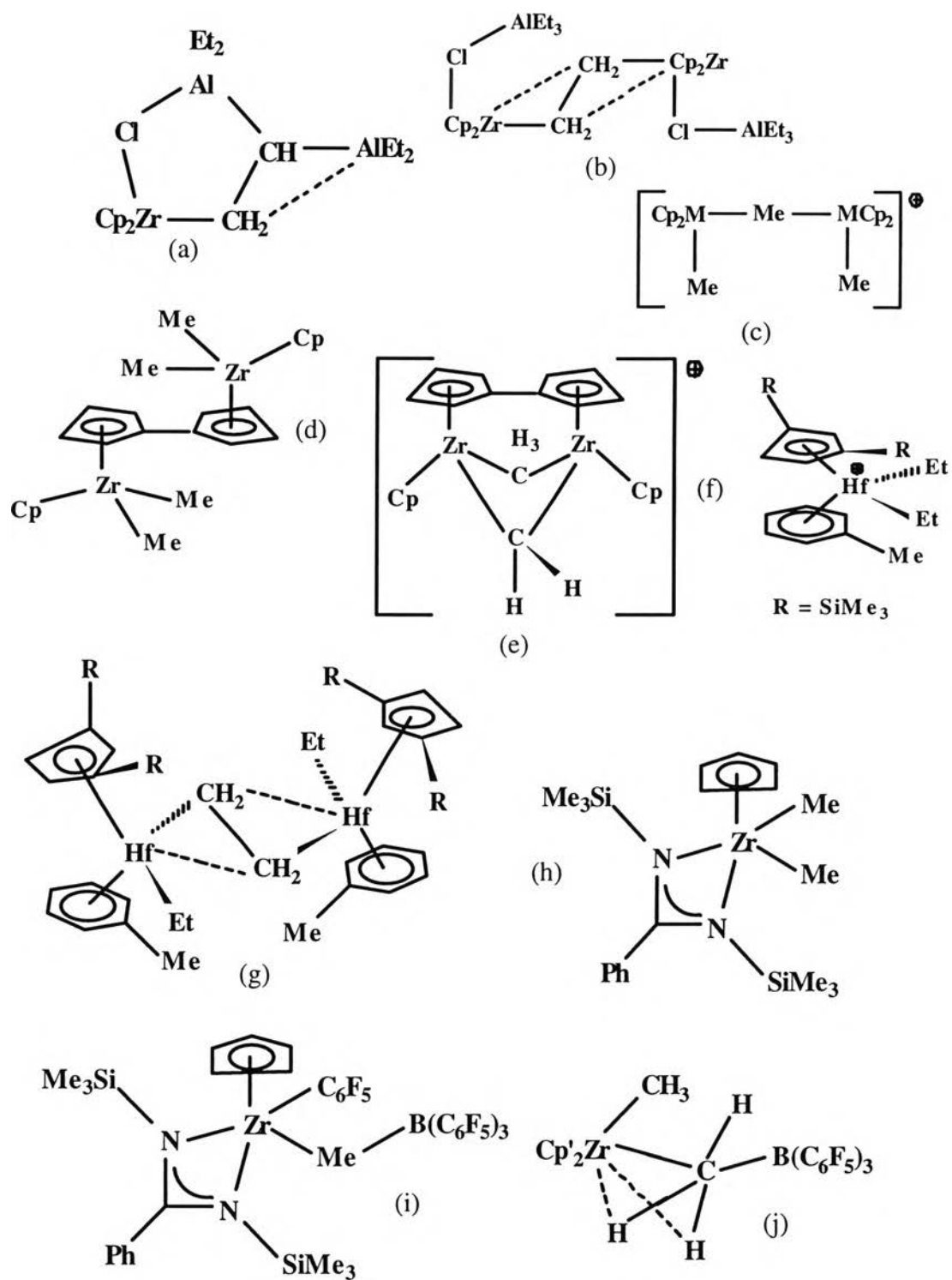
Figure 2.7 Examples of cationic metallocene inactive species (Bochmann, 1996).

reagent has a tendency to eliminate lithium fluoride, an explosive compound, at ambient temperature. The Grinard reagent, on the other hand, can be refluxed in toluene with no risk (Pier and Chives, 1997).

Tris(pentafluorophenyl) borane, $B(C_6F_5)_3$, is in many ways an ideal boron-based Lewis acid, possessing both high Lewis acid strength and stability when compared to the boron trihalides. It is remarkably thermally robust while many fluorinated boron compounds tend to decompose by eliminating BF_3. $B(C_6F_5)_3$ is stable for several days at temperature up to 270 °C. It is also resistant towards oxidation by molecular oxygen and is water tolerant. In terms of Lewis acid strength, $B(C_6F_5)_3$ is a slightly better Lewis acid than BF_3 but not as strong an electron acceptor as BCl_3, as judged by spectroscopic comparison between amine adducts of a number of these boron-based Lewis acids. Finally, it can be prepared base-free (although it is extremely hygroscopic in this form) and it is soluble in many non-coordinating organic solvents.

2.5.2 Reaction of $B(C_6F_5)_3$ with zirconium alkyls

The properties described above led Yang (1991) and Ewen and Edler (1991) to test $B(C_6F_5)_3$ as a cocatalyst for group 4 metallocene-based homogeneous olefin polymerization systems. It has become increasingly apparent that the role of the traditional cocatalyst for this reaction, a complex species prepared from timethylaluminium and water known as methyaluminoxane (MAO), is to serve both as an alkylating agent and a powerful Lewis acid capable of abstracting a methyl group from the metal center and creating the active cationic organometallic species responsible for olefin enchainment. Thus, it was predicted that treatment of dimethyl zirconocenes ('pre-alkylated' catalyst precursors) with a Lewis acid more powerful than the resulting $Cp_2Zr^+CH_3$ cation would lead to highly active olefin polymerization catalysts. Tris(pentafluorophenyl) borane was tagged as

an excellent candidate for playing this role. As shown in Equation 2.4, treatment of a variety of dimethyl zirconocenes with $B(C_6F_5)_3$ leads to cation-like compounds of the general formula $[Cp'_2ZrCH_3]^+[CH_3 B(C_6F_5)_3]^-$.

$$Cp'_2Zr(CH_3)_2 + B(C_6F_5)_3 \xrightarrow[\substack{C_6H_6 \\ or \\ pentane}]{} Cp'_2Zr^+(CH_3) \cdots H_3CB^-(C_6F_5)_3 \quad (2.4)$$

$$Cp' = \eta^5\text{-}C_5H_5$$
$$\eta^5\text{-}1,2\text{-}Me_2C_5H_3$$
$$\eta^5\text{-}C_5Me_5$$
$$\eta^5\text{-}1,3\text{-}(SiMe_3)_2C_5H_3$$