

CHAPTER II

THEORY

To really understand the importance of the so-called “single-site” catalyst, it is necessary to look at the difference between these catalysts and the “multi-sited” Ziegler-Natta type catalysts. In the Ziegler-Natta catalysts, which are heterogeneous, the active metal center occupies a position on the surface of the crystal. Polymerization at the active site is influenced by the electronic and steric environment of the crystal lattice. Because the active centers can occupy a wide variety of lattice sites, they tend to give products with a broad molecular weight distribution (MWD) and also, for example, non-homogeneous comonomer distribution in olefin copolymer.

The example of the Ziegler-Natta catalyst system $\text{MgCl}_2\text{-TiCl}_4/\text{AlR}_3$ is endowed with a very high activity in ethylene polymerization. In the case of the propylene polymerization, the high activity is combined with a low stereospecificity (40-50%).^[1]

Bis(cyclopentadienyl)group IV metal complexes are currently introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins. Ziegler-Natta catalysis means the rapid polymerization of ethylene and α -olefins with the aid and in the coordination sphere of a metal catalyst, operating at low pressures (up to 30 atm) and low temperatures (less than 120°C). The group IV metallocene catalysts make polymers accessible which cannot be produced by conventional Ziegler-Natta catalysts.

From 1984, when the stereoselective polymerization of propylene with zirconocene catalysts was first reported, the synthetic, structural, mechanistic and applied research on metallocene catalysts has been highly visible in organometallic chemistry. A central piece of work in zirconocene catalyzed polymerizations of α -olefins was the elucidation of ligand effects, the correlation of the steric situation at the Cp-ligand with the polymer parameters, such as molar mass, molar mass distribution, comonomer insertion and distribution, and especially the tacticity. With

metallocene catalysts the polymer parameters can be tailored through a rational ligand design at the transition metal center.

The zirconocene complexes are not catalytically active by themselves but require the action of a cocatalyst. The cocatalyst is methylaluminumoxane, abbreviated as MAO. The novelty of metallocene *versus* classical Ziegler-Natta catalysis is best summarized in the word 'single-site catalyst'. This means that the active catalytic sites in the molecular zirconocene species are almost identical, whereas classical Ziegler-Natta catalysts are heterogeneous not just by the phase (as solid state catalysts) but also by having active sites with different environments at corners and edges on the solid surface. Metallocene catalysts are sometimes also termed 'homogeneous' referring both to their solubility and to their single-site character.

Looking more in depth into the chemistry of metallocene based catalyst, significant analogies but also remarkable differences can be identified with the traditional titanium based chemistry. Among the former ones, it has to be mentioned that both titanium and metallocene based catalysis give rise to insertion polymerization, that can be classified as a coordinated ionic reaction with the transition metal bearing a partial positive charge and it occurs through a *cis* coordination of the olefin on the catalytic site.

The most important differences between classical Ziegler-Natta and metallocene catalysts can be summarized as follows:

1. Metallocenes are organometallic compounds that can be completely characterized, both from the chemical and the structural point of view.
2. They are soluble in aliphatic and aromatic solvents.
3. The electronic and steric surrounding of the catalytic center can be much more easily modified in the case of metallocene based catalyst.
4. The chain growth mechanism implies two coordination sites in the case of metallocene based catalyst, while only one is available for the titanium anchored on the MgCl_2 surface.

5. The homogeneity of the catalytic centers, in the case of metallocene based catalyst (single-center catalysts), allows the preparation of polymers with narrow molecular weight distribution and chemical composition^[1].

2.1 Metallocene based catalyst

Metallocenes are organometallic compounds with two cyclopentadienyl ligands (Cp) coordinated to a transition metal, typically titanium, zirconium or hafnium. The general formula Cp_2MX_2 can be used to describe these compounds. The Cp ligands can be substituted by alkenyl, aryl and alkylaryl groups, with fused aromatic or aliphatic rings and bridged through carbon, silicon and germanium atom. The “X” ligands derive either from halogen atoms (typically chlorine) or from hydrocarbons (e.g. methyl or *n*-butyl groups) or from alcohols (e.g. α -binaphthol).

The typical chemical structure of metallocene catalyst is shown in Figure 2.1, where M is the group IVB, VB or VIB transition metals, generally in group IVB (Ti, Zr and Hf). A is bridging atom (usually C, Si atom) or bridging molecule as ethylene, R can be H, alkyl, or hydrocarbon groups and X represents chlorine or other halogens or an alkyl group.

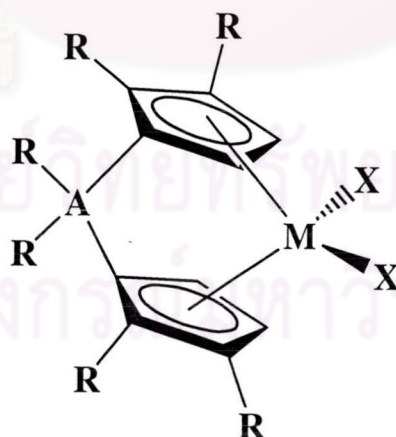


Figure 2.1 Typical chemical structure of a metallocene catalyst.

The use of metallocene as homogeneous polymerization catalysts has dramatically improved the understanding of mechanistic features such as the nature of the active sites and the influence of ligand structure on the regio- and stereoselectivity. One of the many advantages is the controlling of activity, molecular weight, polydispersity and microstructure of the resulting polyolefins by structurally well-defined and on the molecular level modifiable metal complexes.

2.2 Half-metallocene catalyst

It is well known that the many advantages of the metallocene systems generally associated with the bis(cyclopentadienyl) ligand systems. However, they occasionally turn into a disadvantage: the characteristic and highly consistent electronic and steric situation within the bent metallocene unit has long been recognized to cause substantial steric blocking of the metal-centered reaction site.

Enhancement of reactivity is observed when the two ring ligands are “tied back” by a dimethylsilanediyl link as in many Brintzinger-type *ansa*-metallocene complexes. In order to alleviate this steric constraint of the metallocenes, one could utilize, in place of two cyclopentadienyl ligands, one cyclopentadienyl ligand that contains an additional coordinating site X or L tethered to the periphery of the five-membered ring *via* a bridge Z, where X and X' donate a one-electron, L and L' are two-electron ligands (using the neutral ligand formalism), and Z is a covalent bridge of appropriate length (Figure 2.2). Such bidentate ligands may form chelate complexes in which the cyclopentadienyl group and the additional donor group X or L are both interacting with one metal center.

จุฬาลงกรณ์มหาวิทยาลัย

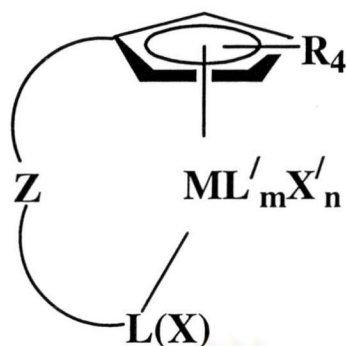


Figure 2.2 General formula for a metal complex containing a bifunctional cyclopentadienyl ligand.

The replacement of one cyclopentadienyl moiety in a bridged bis (cyclopentadienyl) ligand by an amido ligand NR' , connected *via* a bridge Z , results in ligand systems that form complexes differing from both *ansa*-metallocenes and the simple half-sandwich complexes without the link Z (Figure 2.3). The amido group is a three-electron ligand, in contrast to the a five-electron L_2X -type cyclopentadienyl ligand.

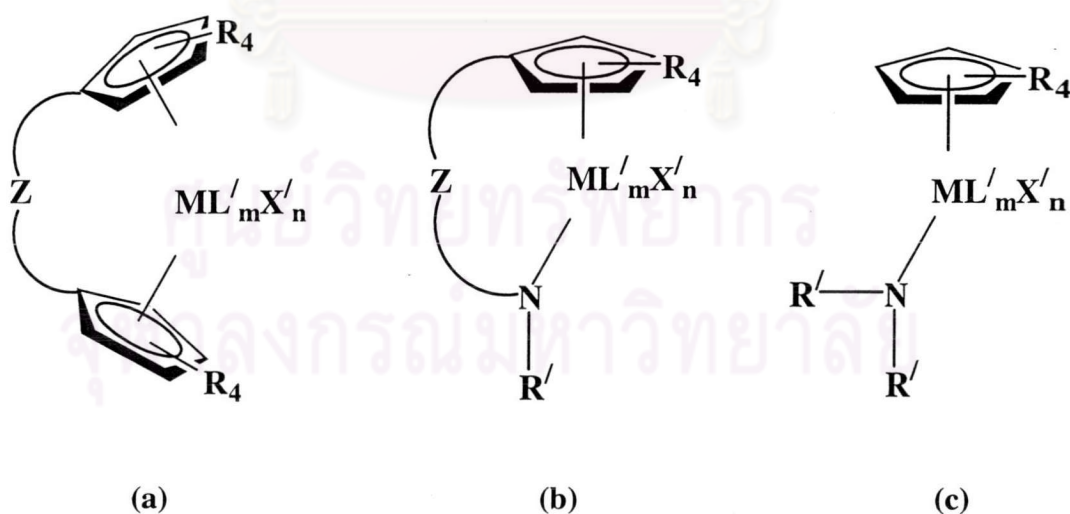


Figure 2.3 Relationship between (a) *ansa*-metallocenes, (b) linked amido-cyclopentadienyl, and (c) half-sandwich amido complexes.

2.3 Non-metallocene catalyst

More recently, some new complexes with non-Cp ligands are also claimed as the catalysts for olefin polymerization. The advances in the design and synthesis of well-defined transition-metal complexes have spurred the rapid development of highly active olefin polymerization catalysts. Thus, quite a few highly active olefin polymerization catalysts based on both early- and late-transition-metal complexes have been developed. Notable examples are nickel complexes with diimine ligands^[11] or phenoxy-imine ligands^[12], iron or cobalt complexes with diimined-pyridine ligands^[13], titanium complexes with diamide ligands^[14], phosphine-imide ligands^[15], zirconium complexes with diamide ligands^[16] or bis(phenoxy)-amine ligands^[17], and tantalum complexes with amide-pyridine ligands. These complexes display activities comparable to those of the group IV metallocene catalysts. These complexes are considered to have more space like constrained geometry catalyst for the monomer coordination as compared with ordinary metallocenes. These complexes may be thus of interest also for the synthesis of copolymers of olefinic monomers.

2.3.1 Late-transition metal catalysts

Early transition metal complexes such as zirconocene catalysts are extensively used for the coordination polymerization of apolar 1-olefins such as ethylene and propylene. These complexes are difficult to handle and incompatible with polar monomers due to the high Lewis acidity of the active cations. Recently, intensive research activities have been focused on late transition metal complexes as polymerization catalysts, although they often only dimerize or oligomerize 1-olefins due to a competing β -hydride elimination reaction.^[18]

Some of the most readily accessible diamido/donor ligands are of the type $[(ArNCH_2CH_2)_2D]^{2-}$, where $D = O^{[19,20]}$, $S^{[20]}$, or NR ($R = H$ or Me)^[21,22] and Ar is a sterically protected aryl such as 2,6- i -Pr₂C₆H₃ or 2,4,6-Me₃C₆H₂. Ligands in which $D = NMe$ are especially attractive in view of the greater steric protection that is exerted by

the substituted central donor, the presence of one lone pair on the donor, and the relative rigidity of the tridentate ligand framework.^[16]

An important advance in late transition metal polymerization catalyst technology was described by Brookhart and co-workers, who showed that Ni(II) and Pd(II) complexes incorporating bulky α -diimine ligands are capable of polymerizing ethylene and α -olefins to high molar mass polymers.^[23-25] Moreover, iron was used as a polymerization active center due to its low cost and ready availability. There have been reported study on highly active ethylene polymerization catalysts based on iron (II) and cobalt(II) bearing 2,6-bis(imino)pyridyl ligands.^[13,26] The design of the Fe and Co catalyst systems is based on the observation that a 14-electron alkyl cation is commonly postulated as the active species for α -olefin polymerization. An example in the use of a Group 8 metal with a neutral tridentate ligand is the bis(imino)pyridine ligand.

2.4 Nitrogen-based ligands

The attendant ligands in polymerization-active metal complexes have four important roles:

- a. Control over the metal coordination number.
- b. Control over the metal coordination geometry.
- c. Control over the formal oxidation state of the metal.
- d. Steric protection of the active site and influence over (stereo) selectivity.

By way of example, consider the series of active zirconium procatalysts A-C (Figure 2.4). The choice of chelating dianionic diamide ligands allows zirconium(IV) dichloro fragments to be stabilized either in a pseudo-tetrahedral environment for A or in distorted trigonal-bipyramidal environments for B and C. Moreover, the choice of an ether or pyridyl bridge influences the relative dispositions of the metal-attached atoms. In the case of B there is a trigonal arrangement of the N,O,N atoms of the

ligand with the oxygen occupying the axial site of the trigonal bipyramid, while in the case of C the N,N,N tridentate chelating ligand binds in a planar arrangement, thereby leaving the chloro ligands to occupy the equatorial sites of the trigonal bipyramid. The ligands present in A, B and C may be represented as $[N^-,N^-]$, *trig*- $[N^-,O,N^-]$, and *planar*- $[N^-,N,N^-]$, respectively.

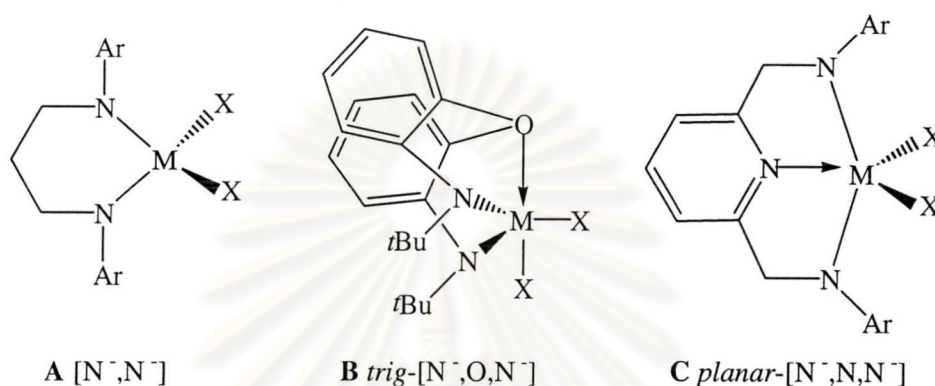


Figure 2.4 Examples of zirconium(IV) procatalysts to illustrate the ligand classifications.^[30]

2.4.1 Amide ligands $[N^-]$

A formal lower electron count ($[(R_2N)_2ZrR]^+$, 10-electron species; compared with 14-electrons for $[Cp_2ZrR^+]$) is likely to result in a more electrophilic and therefore potentially more active catalyst fragment.

A few reports on the use of monodentate amide ligands have appeared, featuring either trimethylsilyl or bulky aryl substituents on nitrogen. Moderate activities ($13 \text{ g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$) are reported for zirconium complex **1** using MAO as a cocatalyst.^[30] The various catalyst precursors are shown in Figure 2.5.

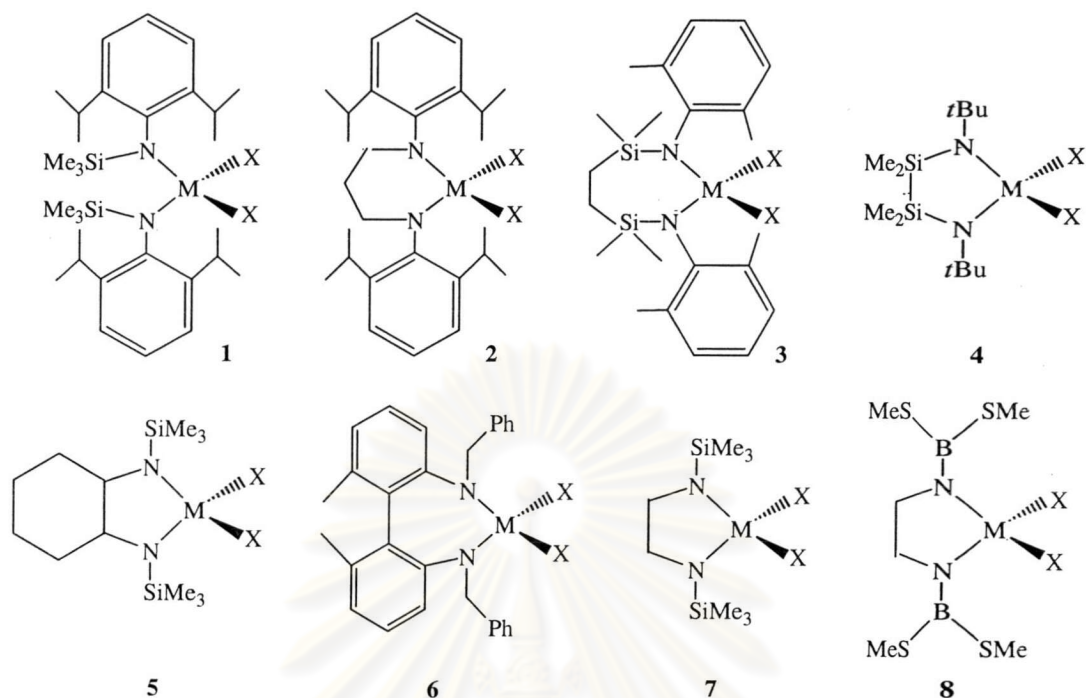


Figure 2.5 Group IV procatalyst containing diamide $[N^1, N^1]$ ligands.^[30]

Olefin polymerization activities obtained with these complexes vary significantly and decrease in the order from **2** to **8**. Activities are very low to low in the case of complexes **7** and **8**. Moderate activity ($13 \text{ g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$) is observed with the biphenyl derivative **6**. Zirconium complex **5** shows moderate activities ($50 \text{ g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$); no polymerization activity data has been given for the titanium analogue. Complex **4**, containing a silicon backbone, was found to be considerably more active ($100 \text{ g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$) than its carbon backbone analogue **7**. A lowering of the electron density on the metal center and an overall stabilizing effect are believed to be the reasons for this “silicon effects”. For the diamide complex **2**, no activity data on ethylene polymerization is disclosed, but α -olefin polymerization results indicate very high activity.

For the titanium complexes, living polymerization of 1-hexene has been reported. The silicon-bridged diamide complexes **3** also form highly active ethylene polymerization catalysts ($990 \text{ g m mol}^{-1}\text{h}^{-1}\text{bar}^{-1}$). Polymerization activity and kinetic profile are dramatically influenced by the chelate ring size. Both systems contain

bulky aryl substituents on the nitrogen donors which probably provide steric protection to avoid attack of the cocatalyst (MAO) on the amide ligand. Such an attack may cause catalyst deactivation either by complete loss of the ligand.

2.4.2 Combination of an amide ligand with other ligands

2.4.2.1 With additional donors $[N^{-1}, Y, N^{-1}]$

Three different systems have been reported to date of a group IV bis(amido) complex with an additional donor Y - that is, an amine, pyridyl, or ether donor - incorporated in the ligand system. The ligand systems *trig*- $[N^{-1}, N, N^{-1}]$ (complex **9**, Figure 2.6) developed by Horton and co-worker and *planar*- $[N^{-1}, O, N^{-1}]$ (complex **13**) developed by Bochmann and co-workers have given moderate activities in the polymerization of ethylene (46 and 40 g mmol⁻¹h⁻¹bar⁻¹ respectively). The ethylene-bridged $[N^{-1}, O, N^{-1}]$ system **12** has been shown to adopt both planar coordination (for X = Me) as well as the trigonal coordination mode (for X = benzyl); no details of ethylene polymerization have been given. The analogous aryl-bridged ligand *trig*- $[N^{-1}, O, N^{-1}]$ (**11**) has shown moderate activities (100 g mmol⁻¹h⁻¹bar⁻¹). Interestingly, an additional pyridyl donor between the amide groups (**10**) affords very high activities (1500 g mmol⁻¹h⁻¹bar⁻¹); in contrast, the titanium analogue has shown only very low activities for the polymerization of ethylene, possibly due to reduction to titanium. A recent example of a zirconium complex containing a $[N^{-1}, N, N^{-1}]$ type ligand (**14**), synthesized by Schrock and co-workers, has been shown to be inactive in the polymerization of 1-hexene, leading to the conclusion that the donor group should ideally be positioned between the amido functionalities.

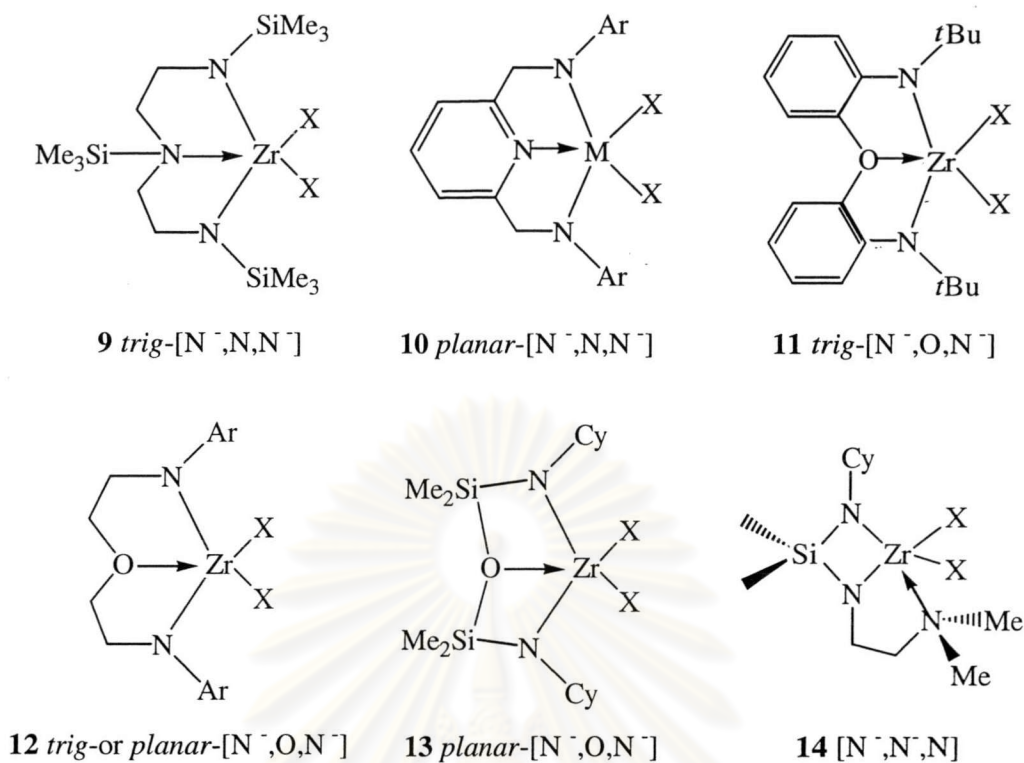


Figure 2.6 Group IV complexes with diamide ligands that contain an additional donor.^[30]

2.4.2.2 With Cp ligands [N⁻, C₅⁻]

An important class of olefin polymerization catalysts has been developed at Dow and Exxon, by combining Cp ligands with an amide functionality [N⁻, C₅⁻] to form a hybrid “half-metallocene”, the “constrained-geometry catalysts”(CGC; **15**, Figure 2.7). These catalyst systems are highly active (1500 g mmol⁻¹h⁻¹bar⁻¹) and are under development for commercial exploitation. The titanium complex **15** (M = Ti, X = benzyl), when activated with MAO, gives good incorporation of 1-hexene comonomer.

Teuben and Green have used a carbon linkage instead of silicon (**16**), and Okuda investigated a series of different Cp analogues (**17**). The copolymerization of ethylene and styrene has also been reported. Like metallocene, these constrained-geometry catalysts have been the subject of several theoretical studies.

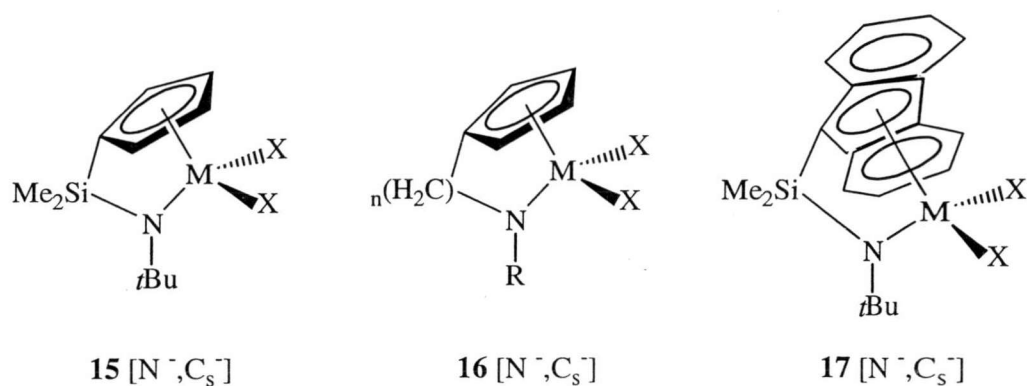


Figure 2.7 Group IV procatalyst with half-sandwich amide [N⁻, C₅⁻] ligands.^[30]

2.4.3 Amidinate ligands [N₂⁻]

An amidinate ligand, a monoanionic six-electron ligand, can formally be regarded as a combination of an amido and an imine donor. Only a few examples have been studied, either with a methyl substituent in the backbone and cyclohexyl groups at nitrogen with a phenyl or *p*-tolyl group in the backbone and SiMe₃ groups at nitrogen (**18**, Figure 2.8). Thus far only moderate activities have been obtained. Polymerization of styrene with these complexes has also been reported. The imine moiety of the amidinate ligand can also be part of an aromatic system, for example a pyridine or pyrimidine ligand, giving aminopyridinato ligands (**19**). The complexes containing these ligands, however, have shown only low activity.

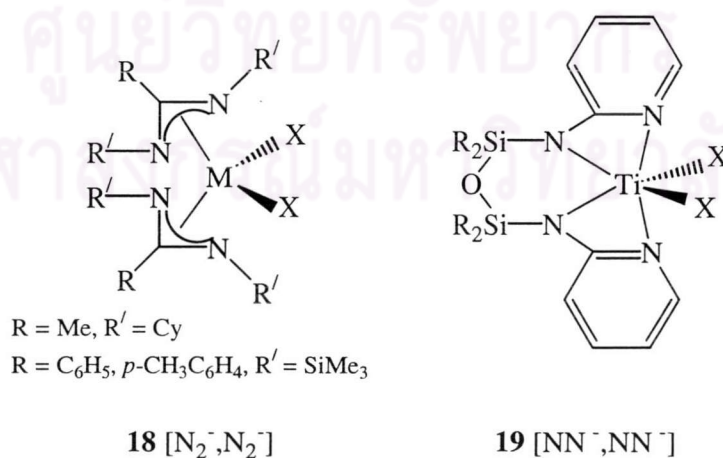


Figure 2.8 Group IV bis(amidinate) procatalysts.^[30]

2.4.4 Combinations of an amidinate ligand with other ligands

Electronically related to the constrained-geometry catalyst combinations of amidinate ligands with other ancillary ligands (**20-22**, Figure 2.9) have been studied. Moderate activities have been obtained, using either the dihalide precursor **20** in combination with MAO or the dimethyl precursor with $B(C_6F_5)_3$. Polymerization results for propylene and 1-butene show remarkably high activities using catalyst **21**. Complex **22** shows moderate activity ($80 \text{ g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$) for ethylene polymerization, whereas the analogous zirconium complex was reported to give very low activity.

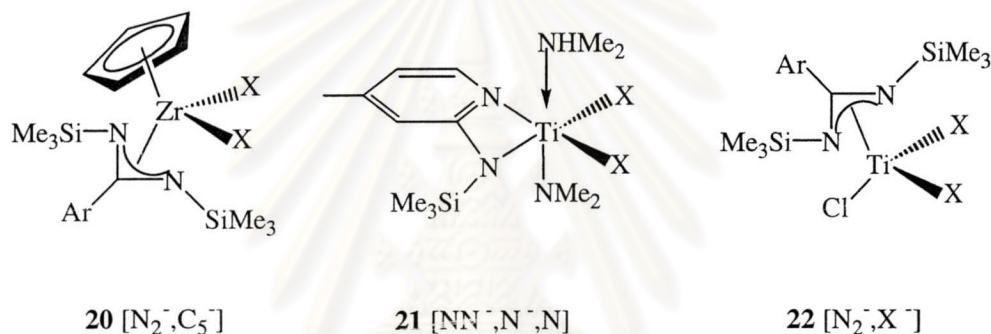


Figure 2.9 Group IV mono(amidinate) complexes with other ancillary ligands.^[30]

2.4.5 β -Diketimate ligands $[N_2^-]$

In 1993 Jordan and co-workers reported the synthesis of cationic d^0 group IV metal alkyl complexes incorporating tetraaza macrocyclic ligands and their application as olefin polymerization catalysts. These β -diketimates can be regarded as higher homologues of amidinate ligands, as depicted in Figure 2.10. The Zr complex **23** is about 30 times less active than $CpZrCl_2$, thereby falling in the category of moderately active catalysts. Well-defined cationic complexes of type **24** have been reported to exhibit only very low activity for the polymerization of ethylene.

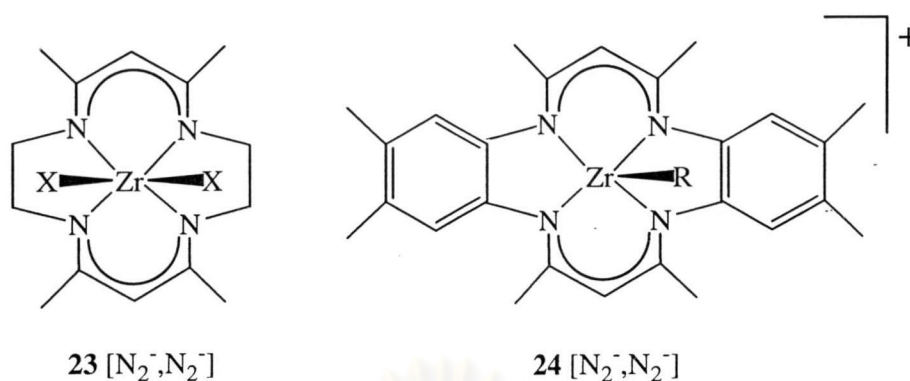


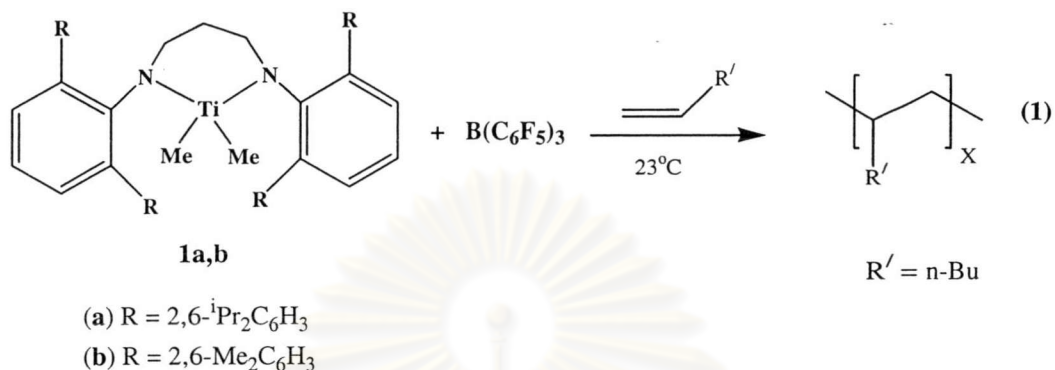
Figure 2.10 Group IV procatalysts with bis(diketimate) ligands.^[30]

2.5 Living Polymerization

Living polymerization is of practical importance in the synthesis of monodisperse polymers and tailor-made polymers such as terminally functionalized polymers and block copolymers. A living polymer is formed in the polymerization system where no chain – terminating processes are present (rate of β -hydride elimination is slower (or absent) than the rate of chain transfer to aluminum, chain growth proceeds without chain termination). A relationship between M_n and time is linear and if the rate of initiation is comparable to, or faster than, the rate of propagation, a narrow molecular weight distribution is obtained.

The first example of a living polyolefin with a uniform chain length was disclosed by Dol *et al.*, who used a soluble Ziegler-Natta catalyst of $V(acac)_3$ ($acac =$ acetylacetonato) and $Al(C_2H_5)_2Cl$ at temperatures below $-65^\circ C$ for the polymerization of propylene. The living polypropylene end of a vanadium-carbon bond was found to react with additives such as I_2 and CO to give terminally functionalized polypropylenes. In addition, this new type of living polymerization has been applied to the synthesis of well-defined block copolymers such as polypropylene-polyethylene, polypropylene-polystyrene, polypropylene-poly(methyl methacrylate). However, the activity of the catalyst was relatively low for the synthesis of living polypropylene.

The living polymerization of an aliphatic α -olefin at room temperature is achieved by complexes of the type $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{TiMe}_2$ ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$; $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), when activated with borane cocatalyst.



The measurement of the time dependence of the polymerization of 1-hexene with the catalyst system **1b**/ $\text{B}(\text{C}_6\text{F}_5)_3$ in a 50:50 mixture of toluene/1-hexene (Figure 2.11) gives a linear relationship between M_n and time, indicating that the system is living. A significant increasing in viscosity and the declining monomer to catalyst ratio are likely responsible for this observation. If additional monomer and solvent are added periodically, the molecular weights continue to increase ($>500,000$) with no change in the polydispersities ($M_w/M_n = 1.06\text{-}1.07$).

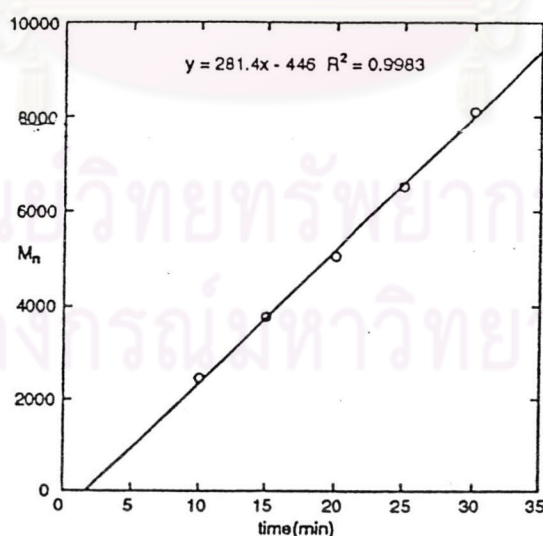
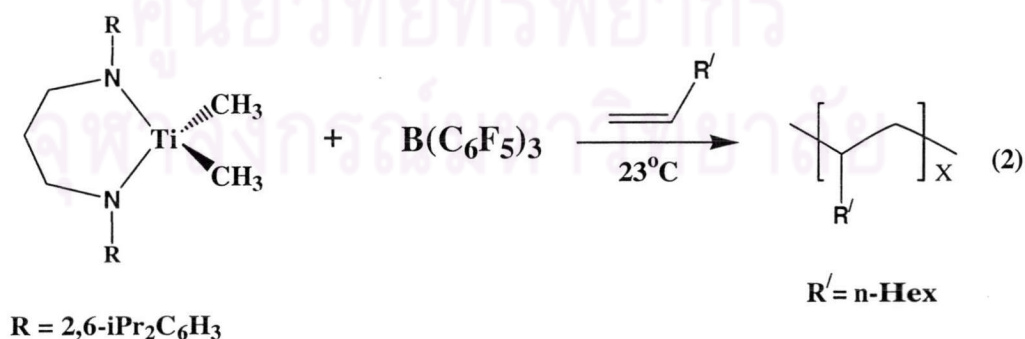


Figure 2.11 Time dependence on M_n for the polymerization of 1-hexene with **1b**/ $\text{B}(\text{C}_6\text{F}_5)_3$.

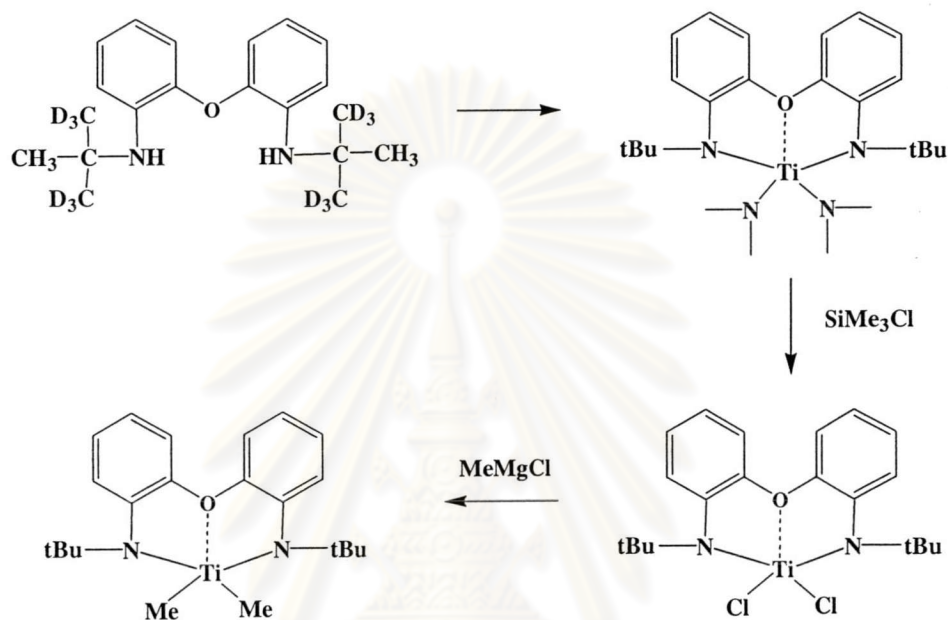
Moreover, the zirconium complexes with 2,2'-ethylenebis(N,N'-(triisopropylsilyl)anilino) ligand conducted the living polymerization of 1-hexene at -10°C , $[\eta^1:\eta^3 - \text{tert} - \text{butyl} (\text{dimethylfluorenylsilyl}) \text{ amido}] - \text{dimethyl} - \text{titanium} ([\text{t-BuNSiMe}_2\text{Flu}]\text{TiMe}_2)$ also conducted living polymerization of propylene and 1-hexene combined with tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) at -50°C in a highly regiospecific manner^[27].

Hagira *et al.*^[28,29] used a Ni(II)- α -diimine catalyst to polymerize syndiotactic polypropylene, when they switched to a borate cocatalyst and lowered the reaction temperature to -50°C , the living polymerization was found. Polypropylene with $M_n = 20,000 \text{ g/mol}$, $MWD = 1.15$ and catalyst activity of $590 \text{ kg PP/mol Ti.h}$ were reported. For poly(1-hexene), low activity ($0.152 \text{ kg polymer/mol Ti.h}$), $M_n = 26,000 \text{ g/mol}$ and $MWD = 1.10$ were found.

Scollard and McConville^[30] reported the living polymerization of α -olefins by chelating diamide complexes of titanium. When activated by MAO, the catalysts showed high activities in the polymerization of 1-hexene. Replacing MAO with a borate anion resulted in the living polymerization of α -olefins at room temperature. Fairly high activities ($750,000 \text{ g mol}^{-1}\text{h}^{-1}$), M_n values of up to $160,000$ and narrow MWD (1.05 to 1.09) were achieved.



Baumann *et al.*^[31] reported on the Ti and Zr complexes that contain the tridentate ligand : [NON]ZrMe₂. These catalyst complexes can be activated by B(C₆F₅)₃ and used for ethylene polymerization (activity 800,000 g mol⁻¹h⁻¹) and 1-hexene (activity 200,000 g mol⁻¹h⁻¹). Molecular weight for the poly(1-hexene) is reported to be around 45,000 g/mol and the MWD = 1.2.



Scheme 2.1 [NON]ZrMe₂ catalyst for ethylene and hexene polymerization.

2.6 Cocatalyst and initiating step in polymerization

Cocatalysts are the key to the activity of the metallocene. They can be classified into 2 main groups; aluminum and boron compound cocatalysts.

2.6.1 Aluminum compound cocatalyst

Methylaluminoxane (MAO) is the famous cocatalyst in this group. It is the product of a careful reaction between trimethylaluminum and water (from a hydrated inorganic salt; Al₂SO₄.16H₂O, CuSO₄.5H₂O, FeSO₄.7H₂O). From many different analytical investigations, cryoscopic measurements, GPC and NMR analysis, one can hypothesize that the MAO structure is composed of a mixture of linear or cyclic oligomers of MeAlO units or a metallocene in a host-guest complex as in Figure 2.12.

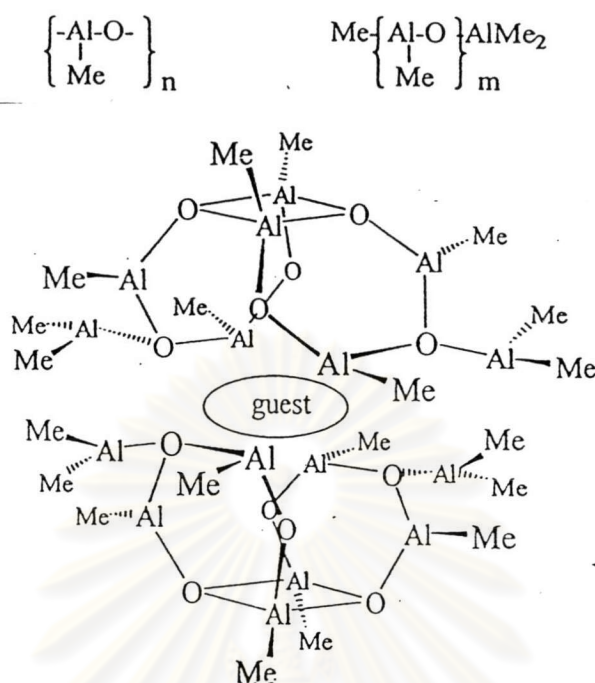
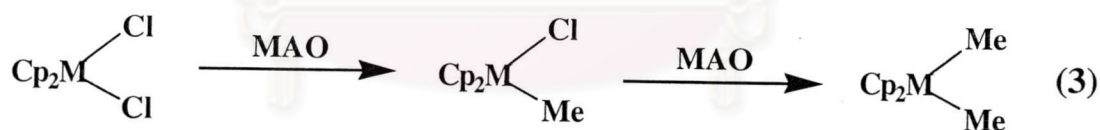
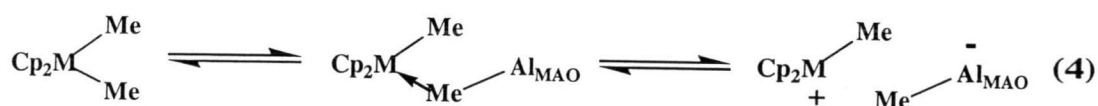


Figure 2.12 The postulated MAO structure.

The first function of the MAO is the alkylation of the halogenated metallocene complex. Monomethylation takes place within seconds, and an excess of MAO leads to dialkylated species:



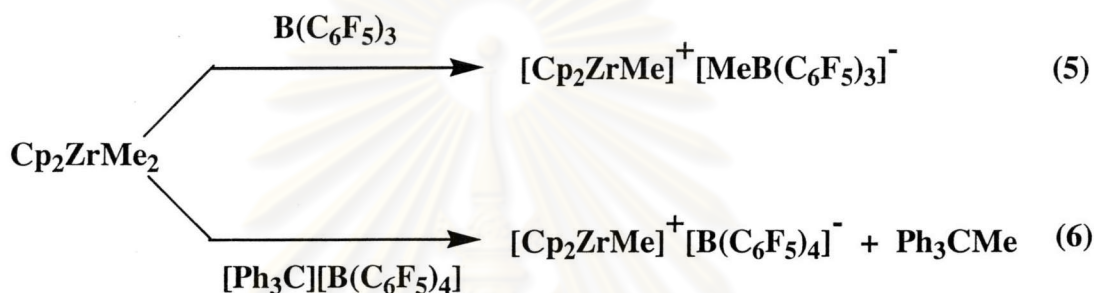
It is generally accepted that MAO is an oligomer compound with a molecular weight between 1,000 and 1,500 g/mol. It would appear as if the MAO complex can seize a methyl anion, a Cl^- or an OR^- from the metallocene, forming an AlL_4^- anion which can distribute the electron over the whole cage, thus stabilizing the charged system:



The formed cationic $\text{L}_2\text{M}(\text{Me})^+$ is generally regarded as the active center in olefin polymerization.

2.6.2 Boron compound cocatalyst

Other bulky anionic complexes which show weak co-ordination, such as borane $\{B(C_6F_5)_3\}$ and borates ($[Ph_3C][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$), play an increasing role too. This is evidenced by the formation of highly metallocene catalysts when using anionic counterions such as tetraphenyl borate $(C_6H_5)_4B^-$, carborane or fluorinated borate. Typically cation metallocene complexes can be formed by reactions of perfluorinated triphenylborane $\{B(C_6F_5)_3\}$ or trityltetrakis (pentafluorophenyl)borate($[Ph_3C][B(C_6F_5)_4]$):

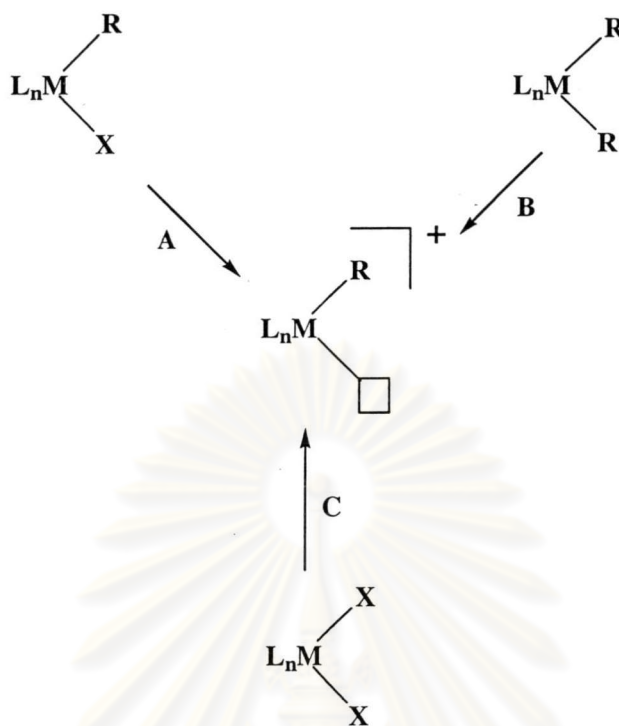


Whereas the ratio of MAO to metallocene needs to be around 5,000:1 for active catalyst systems, the ratio of borate to metallocene is 1:1. On the other hand, the borate system is very sensitive to poisons and decomposition and must be stabilized by small amounts of aluminum alkyls.

A further function of MAO is the reactivation of inactive complexes formed by hydrogen transfer reactions. In solution, the combination of MAO and metallocene leads to fast complexation and methylation, followed by the evolution of methane and a catalytically inactive $M-CH_2-Al$ complex. This complex reacts with MAO to form $Zr-CH_3^+$ and $Al-CH_2-Al$ structure, which explains why a large excess of MAO is required.

2.7 The active site

It is generally agreed that the catalytically active species in olefin polymerization is a coordinatively unsaturated cationic alkyl complex $[L_nMR]^+$. To generate such species several methods can be employed; three different routes (A, B and C) are shown in Scheme 2.2.



Scheme 2.2 Three different routes to the catalytically active species $[L_nMR]^+$
□ represents the site of coordinative unsaturation.

Route A involves the abstraction of an anionic ligand (e.g. a halide) and its substitution for a “noncoordinating” anion by a salt elimination. Common reagents are $\text{Na}[\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$ or silver salts such as AgBF_4 or $\text{AgOSO}_2\text{CF}_3$ (AgOTf) for the late transition metals.

Route B involves the abstraction of an alkyl ligand or, more strictly, an alkyl anion. Reagents used for these ligands are, for example $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{H}(\text{OEt}_2)_2][\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$. Whereas the trityl reagent is an abstracting agent, the anilinium salt and the acid remove the alkyl ligand by protonation. In the case of $\text{B}(\text{C}_6\text{F}_5)_3$ the alkyl ligand is only partly abstracted leading to “cation-like” catalytic species.

Route C is a combined alkylation and abstraction process, which can be achieved by treating a dihalide precatalyst first with an alkylating species and then with one of the aforementioned alkyl-abstracting agents, for example a

trialkylaluminum compound followed by $B(C_6F_5)_3$. Some reagents can perform both processes, for example, alkylaluminumoxane (MAO).

2.8 Possible chain propagation and transfer pathways in polymerization

2.8.1 Propagation step

There are three basic mechanisms suggested for the insertion of olefin into a transition metal alkyl bond in metallocene catalyst^[32], shown in Figures 2.13-2.15. These mechanism are:

1. The direct insertion mechanism proposed by Cossee and Arlman.
2. The metathesis mechanism proposed by Green and Rooney.
3. The modified Green-Rooney mechanism proposed by Brookhart and Green.

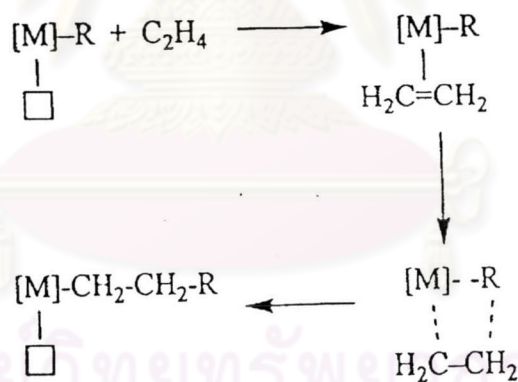


Figure 2.13 Direct insertion mechanism (\square is vacant coordination site).

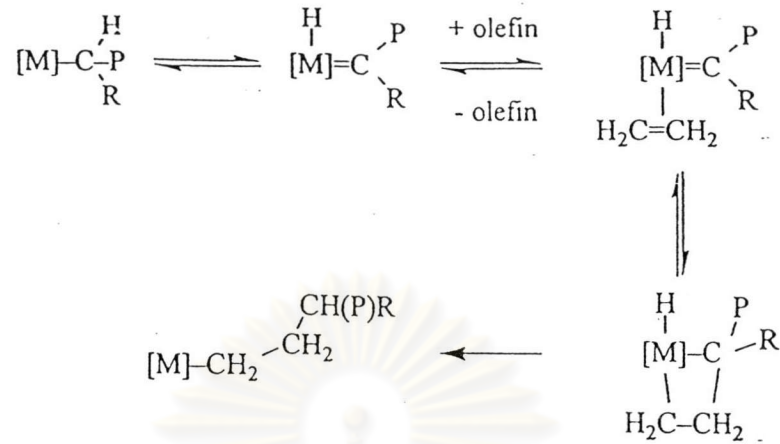


Figure 2.14 Metathesis mechanism.

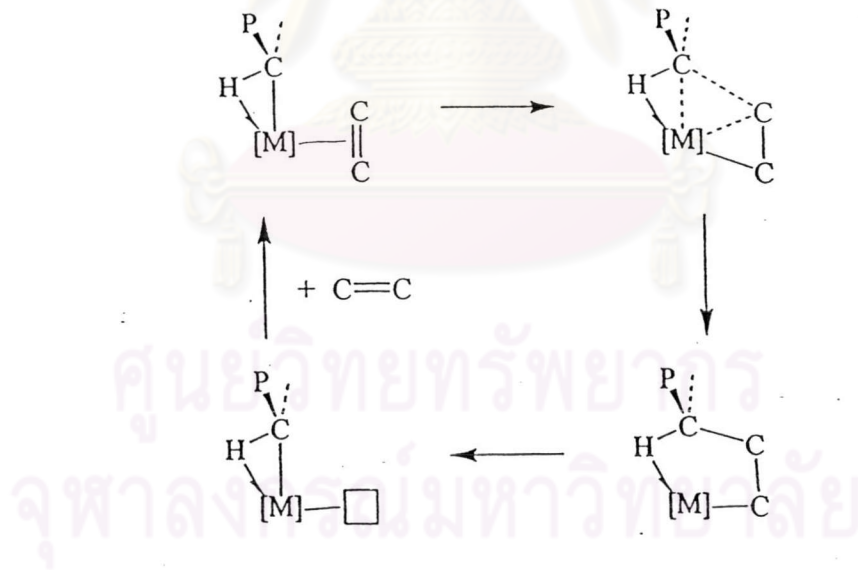
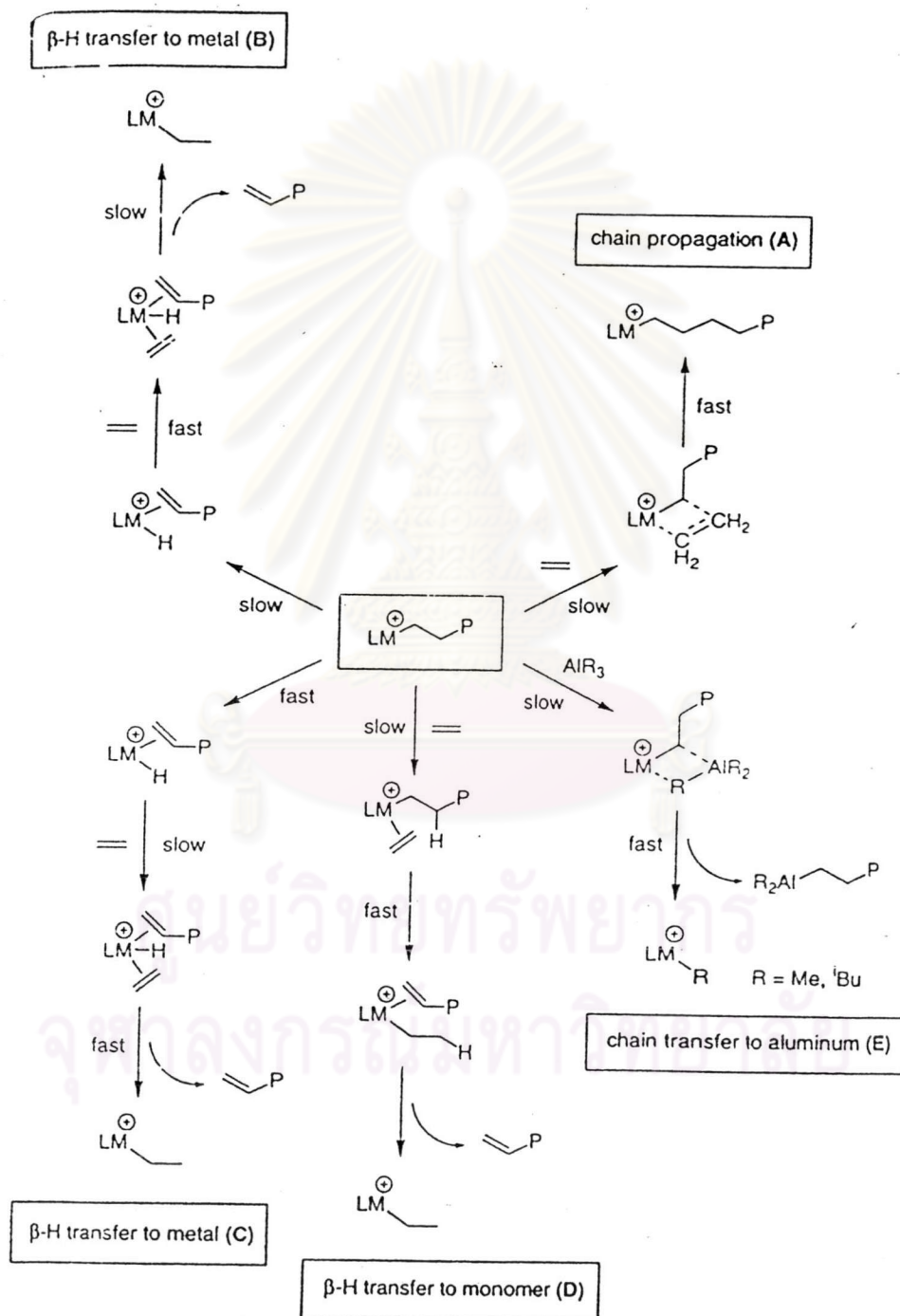


Figure 2.15 Modified Green-Rooney mechanism.

2.8.2 Chain transfer and termination steps

Scheme 2.3 shows the polymerization mechanism, that is, the chain propagation and the possible chain-transfer pathways.



Scheme 2.3 Possible chain propagation and transfer pathways.

In pathway **A**, a Cossee-type propagation mechanism is assumed, involving migratory insertion of ethylene into a metal alkyl bond, whereby the rate has a first-order dependence upon the ethylene concentration.

Four different chain-transfer pathways can be distinguished. Two involve kinetically distinct β -H transfer to metal processes (**B** and **C**), a third β -H transfer to monomer (**D**), and a fourth chain transfer to aluminum (**E**).

β -H transfer to metal of type **B** is a common chain-transfer process, especially for late transition metal catalysts. This β -H elimination reaction is unimolecular, that is, independent of monomer concentration, provided that the subsequent step, the associative displacement of the polymer chain by monomer, is fast and therefore is not the rate-determining step.

If this is not the case, this chain-transfer process becomes a β -H transfer to metal of type **C**, which is kinetically indistinguishable from β -H transfer to monomer (**D**). These chain-transfer pathways are both bimolecular, that is, first order in monomer, and the latter (**D**) has been postulated previously for certain metallocene catalysts.

The fourth, less common chain-transfer reaction is chain transfer to aluminum (**E**). This process has also been observed for Ziegler-Natta systems, group 4 metallocenes, and lanthanocenes and is dependent upon the alkyl aluminum concentration. This pathway involves formation of an alkyl-bridged M--Al species, which allows the growing polymer chain to be exchanged for a new alkyl group, while a vacant site is still available at the metal center.

In general, β -H-transfer reactions, to the metal (**B** and **C**) or the monomer (**D**), give one unsaturated chain end per polymer chain (vinyl end groups), whereas chain transfer to aluminum (**E**) results in fully saturated polymer chains.

2.9 Catalyst activities

Catalyst activities are highly dependent upon the precise reaction conditions, including stirring rate and the configuration of the reactor. Also, often little or no information is given about the kinetic profile or lifetime of the catalyst. Information about the catalyst's kinetic profile is very useful in allowing the most appropriate operating conditions to be chosen. For example, solution-phase catalysts generally require shorter reactor residence time than for a supported gas-phase catalyst.

The activity available in the literature is in units of $\text{g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$ and the rating of activity ranging from very low to very high, as shown in Table 1.

Table 1. Rating of catalyst activity

Rating	Activity [$\text{g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$]
very low	less than 1
low	1-10
moderate	10-100
high	100-1000
very high	more than 1000

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย