

CHAPTER II

LITERATURE REVIEW

2.1 MgCl₂-Supported Titanium Catalyst

A large number of patents and scientific literature describing transition metal catalysts for olefin polymerization have appeared since the discoveries by Ziegler, Natta, and other workers (Boor, 1979; Yermakov *et al.*, 1981; and Mulhaupt, 1995). The success in polymerization has been improved over the last three decades, particularly as improved transition metal catalysts to obtain high efficiency of polyolefin production.

Voluminous excellent literatures regarding the development of polyolefin catalysts exist. The extent of development of supported and unsupported catalysts was shown by Pino and Mulhaupt (1980). In Europe and the United States, transition metal catalysts for olefin polymerization have been used since the early 1950s (Table 2.1). The main problem of the initial catalysts was the yield of polymer in low-pressure processes was very low. So the research on these catalysts to improve activities has been followed and advancement in titanium catalysts resulted from many efforts to form supported catalysts on various materials (Table 2.2).

The high activity catalyst preparation methods were described by Karol (1984) and the commercial catalyst technology was summarized as "state-of-the-art" by Hsieh (1984). Many techniques can be used in the catalyst preparation, such as mechanical or chemical treatment of MgCl₂ with TiCl₄. Since the nature of the active sites is still poorly understood, there has been much diversification in methods of catalyst preparation, especially in recent years. Furthermore, the success in improving the quality of the polymers with catalysts in terms of polydispersity, stereoregularity, and

Table 2.1 Early discoveries of low pressure linear polyethylene
(Welch and Hsieh, 1993).

Research group	Catalysts	Date	Density(g/cm ³)
Alex Zletz, Standard Oil of Indiana	Nickel oxide on activated carbon Molybdenum oxide on alumina	Early 1950	0.960
J. P. Hogan and R. L. Banks, Phillips Petroleum Co.	Chromium oxide on silica alumina	1951	0.95-0.97
Karl Ziegler et al., Max Planck Institute for Coal Research	TiCl ₄ + R ₃ Al	Late 1953	0.945

Table 2.2 Early supported catalysts (Welch and Hsieh, 1993).

Patent no.	Date	Company	Catalyst preparation
BP 841,822	1955	British Petrochemicals	TiCl ₄ reduced by aluminium alkyls in the presence of solids such as MgCO ₃
U.S. 3,153,634	1956	Sun Oil	TiCl ₄ was adsorbed on SiO ₂ /Al ₂ O ₃ and reduced
U.S. 2,980,662	1956	Sun Oil	Ti compounds reduced in the presence of solid NaCl, FeCl ₃ , AlCl ₃ , GaCl ₃ , etc.
BP 877,457	1957	Sun Oil	TiCl ₄ reduced in the presence of inorganic compounds

morphology has had a rapid pace. The development of catalyst for polymerization of propylene will be discussed in the following paragraph (Yang, 1994):

“MgCl₂ was commonly used as a support and seem to be the most effective on the catalyst performance (Galli *et al.*, 1984). Many techniques to improve the effectiveness and activation of the support have been researched and documented (Karol, 1984; Hsieh, 1984; Choi *et al.*, 1985). These techniques include:

1. Mechanical grinding or Ball milling of MgCl₂ support.
2. Precipitation of MgCl₂-ROH solution.
3. Derivation from MgCl₂-rich supported material.”

The mechanical grinding technique of MgCl₂ has been widely investigated (Dumas and Hsu, 1984; Barbe *et al.*, 1987). The preparation technique depended on the required stereospecificity for polymerization. However, the effects of grinding are to reduce the crystal size of MgCl₂, create rotational disorders of Cl-Mg-Cl layer (Barbe *et al.*, 1987), and disturb the structure of the crystal. The MgCl₂-supported Titanium catalysts could form complex surface that provides potential active centers. Moreover, The MgCl₂-supported TiCl₄ catalyst with co-milling with a Lewis base will give a high stereospecificity in olefin polymerization. The most extensively used Lewis base is ethyl benzoate. The surface complexes between TiCl₄ and magnesium atoms were stabilized by ethyl benzoate (Barbe *et al.*, 1987). In addition, ethyl benzoate is believed to help break down the crystal structure of MgCl₂. Some patent examples are presented in Table 2.3.

Due to the difficulties in controlling catalyst morphology with the mechanical grinding of MgCl₂ techniques (Hsieh, 1984), the precipitation of MgCl₂-ROH solution technique has been of interest in recent years. MgCl₂ is soluble in organic solvents such as alcohol and alkanes, therefore a mixed solvent of alkane and alcohol is generally used and MgCl₂ is precipitated out

by the addition of TiCl_4 . This technique makes it possible to get high performance catalysts with a controllable morphology. Some patent examples are given in Table 2.4.

Problems with the mechanical technique, as mentioned earlier, caused continued efforts to obtain MgCl_2 -rich support materials. The reactions of magnesium based precursors, such as Grignard reagents, alkyl magnesium alkoxides, magnesium diaryls, and magnesium dialkoxides with appropriate chlorinated compounds are very finely divided. MgCl_2 -rich supported materials catalysts obtained by reacting TiCl_4 with Grignard reagents and alkyl magnesium alkoxides (Haward *et al.*, 1973; Boucher *et al.*, 1974) have been reported to have high activity for ethylene polymerization. With the use of a proper Lewis base, both activity and stereoregularity could be achieved. Some patent examples are shown in Table 2.5.

Table 2.3 Examples of ball milling catalysts (Yang, 1994).

Patent no.	Date	Company	Catalyst system
EP 45,977	1982	Montedison	$(\text{MgCl}_2 + \text{phthalicanhydride} + \text{TiCl}_4)_{\text{milled}}$ + $\text{ClCH}_2\text{CH}_2\text{Cl}$ -TEA+ $\text{PhSi}(\text{OEt})_3$
JP 63,156,806	1988	Mitsubishi	$(\text{MgCl}_2 + \text{diheptylphthalate})_{\text{milled}}$ + TiCl_4 + heptane -TEA(prepolymerization)/ $\text{Me}_3\text{CsiMe}(\text{Ome})_2 + \text{AlCl}_3$ -TEA
JP 63,175,006	1988	Toho Titanium	$(\text{Mg} + \text{I}_2 + \text{BuCl})/\text{dibutylphthalate} + \text{TiCl}_4$ + Mg stearate) _{milled} + $(\text{TiCl}_4 + \text{toluene})$ - $(\text{TEA} + \text{TMPIP})$
JP 02,145,605	1990	Toho Titanium	$[(\text{Mg} + \text{I}_2 + \text{BuCl}) + \text{dibutylphthalate}]_{\text{milled}}$ / TiCl_4 -TEA+1,8-epoxy-p-methane

Table 2.4 Examples of precipitation catalysts (Yang, 1994).

Patent no.	Date	Company	Catalyst system
EP 86,472	1983	Montedison	(MgCl ₂ +EtOH+TiCl ₄ +diisobutylphthalate)/ TiCl ₄ -TEA+2-amino-2-methyl-1-propanol
EP 86,644	1983	Mitsui	(MgCl ₂ +EtOH+kerosene+emasol)/ TiCl ₄ diisobutylphthalate/ TiCl ₄ (TEA+(OEt) ₃ P)
US 4,710,482	1987	Shell	(MgCl ₂ +MeOH)+Mg/MeOH+i-PrOH/diisobutylphthalate+TiCl ₄ +PhCl/phthaloylchloride(TEA+Ph ₂ Si(OMe) ₂)
JP 01,256,503	1989	Toho Titanium	(MgCl ₂ +ethyl-p-anisate+decane+Ti(OBu) ₄ +2-ethylhexanol+heptane/dibutylphthalate+heptane/TiCl ₄ (TEA+Ph ₂ Si(OMe) ₂)
JP 0,280407	1990	Showa Denko	(MgCl ₂ +2-ethylhexanol+decane)+phthalicanhydride/TiCl ₄ /diisobutylphthalate/TiCl ₄ -TEA+1,3-dimethoxy-1,1,3,3-tetraisopropyldisiloxane

Table 2.5 Examples of MgCl₂-rich catalysts (Yang, 1994).

Patent no.	Date	Company	Catalyst system
EP 245,854	1987	Sumitomo	BuMgCl+Bu ₂ O+Ti(OBu) ₄ +PhOH+ heptane/diisobutylphthalate+PhCl/ Bu ₂ O+TiCl ₄ +PhCl-TEA+PhSiEt ₃
WO 8,706,945	1987	Toho Titanium	Mg(OEt) ₂ +toluene+TiCl ₄ /dibutyl- phthalate/toluene/TiCl ₄ +toluene/ heptane-TEA+PhSi(OEt) ₃
BE 1,000,160	1988	Neste Oy	(Et ₂ Mg/sec-BuMgBu+Ph ₂ Si(OH) ₂)+ TiCl ₄ +diisobutylphthalate/TiCl ₄ - TEA+Ph ₂ Si(OMe) ₂
DE 3,730,022	1989	BASF	(C ₈ H ₁₇ MgBu+SiO ₂ +heptane) _{milled} /HCl/ EtOH/TiCl ₄ +dibutylphthalate/TiCl ₄ +PhEt-TEA+MeC ₆ H ₄ Si(OMe) ₃ +PP
DE 3,730,022	1989	Idemitsu	[Mg(OEt) ₂ +dibutylphthalate]+TiCl ₄ / MeOCMe ₃ +Al(CH ₂ CHMe ₂) ₃ + Heptane-Al(CH ₂ CHMe ₂) ₃ +dicyclo- hexylphthalate
US 4,876,230	1990	Fina	[Mg(OEt) ₂ +TiCl ₄ +toluene]/dibutyl- Phthalate/TiCl ₄ +toluene-TEA+ DIBDMS

2.2 Cocatalysts

The effects of cocatalysts on the polymerization are very important. Chareonsuk, 1995 showed the influences of the concentration of alkylaluminum on the polymerization kinetic profile of ethylene polymerization (Figure 2.1). The effects also depended on the type of alkyl and the ratio of Al/Ti (Chareonsuk, 1995) and showed a maximum at Al/Ti c.a. 50 (Figure 2.2).

In the polymerization of propylene, Barbe *et al.* (1987) found that the initial rate increased with increasing triethylaluminum concentration followed by increasing decay rate in MgCl₂-supported TiCl₄ with AlEt₃ catalyst system.

The reduction in rate with increasing Al/Ti ratio after reaching the maximum rate was caused by the progressive over-reduction of titanium (Boor, 1979; Riechert, 1983). Furthermore, Kim *et al.* (1990) and Tiat *et al.* (1990) observed that the decrease in rate was due to competitive adsorption between cocatalyst and monomer on the same site.

The concentration of the alkylaluminum also affected the stereospecificity of the catalyst. Galli *et al.* (1984) reported that the stereospecificity was enhanced with increasing Al/Ti ratio up to 50 in the TiCl₄/MgCl₂-AlEt₃ catalyst system. It was known that the internal electron donor could be extracted by alkylaluminum which leads to a reduction of isotacticity (Busico *et al.*, 1985; Galli *et al.*, 1984). In addition, Xu *et al.* (1997) observed the same effect in the TiCl₄/DNBP/MgCl₂-AlEt₃ catalyst system. The equilibrium reactions (Scheme 1) were proposed by Sacchi *et al.* (1991) to suggest that the electron donor coordinating with active sites could be extracted by AlEt₃ and these reactions were reversible.

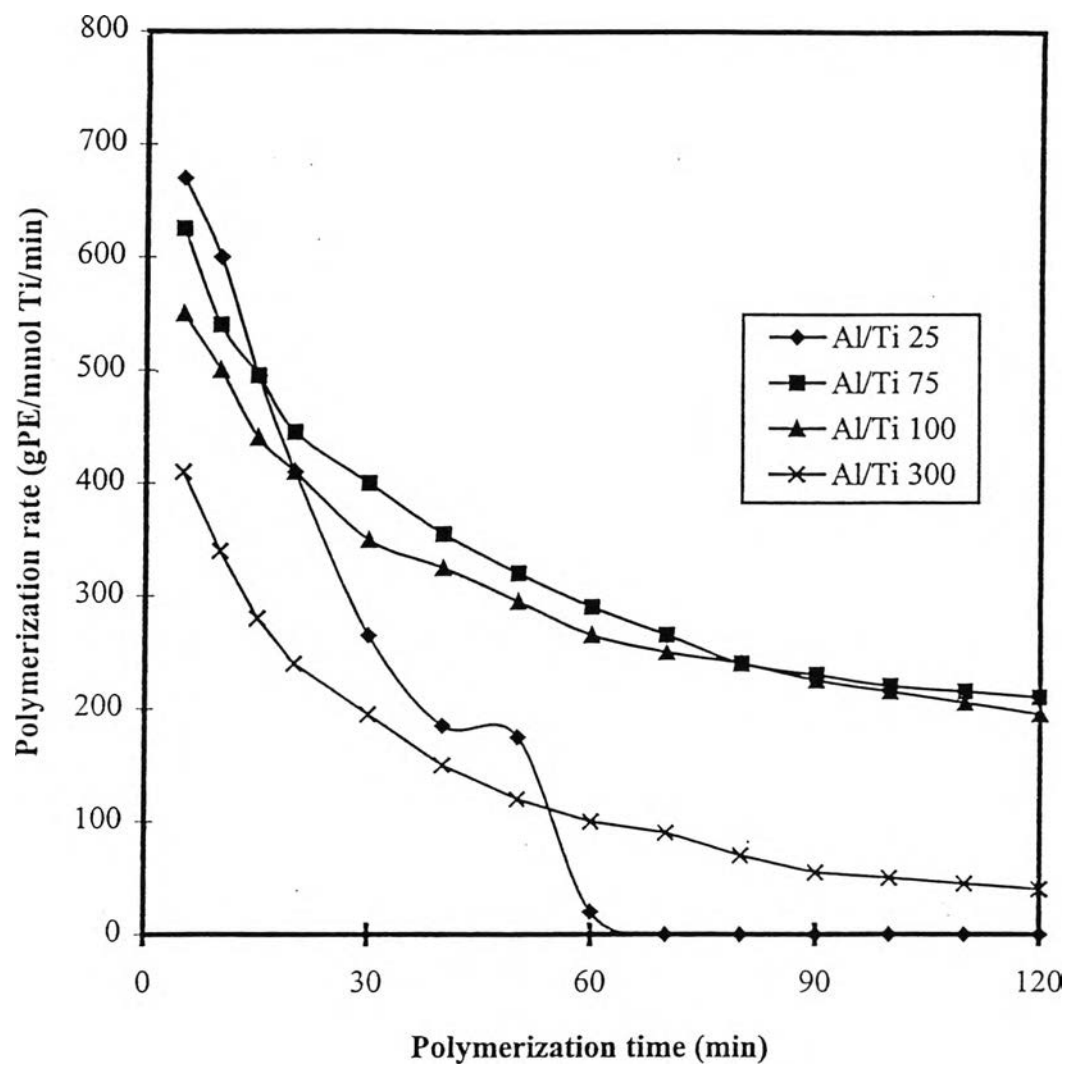


Figure 2.1 Effect of Al/Ti ratio on polymerization rate (Chareonsuk, 1995).

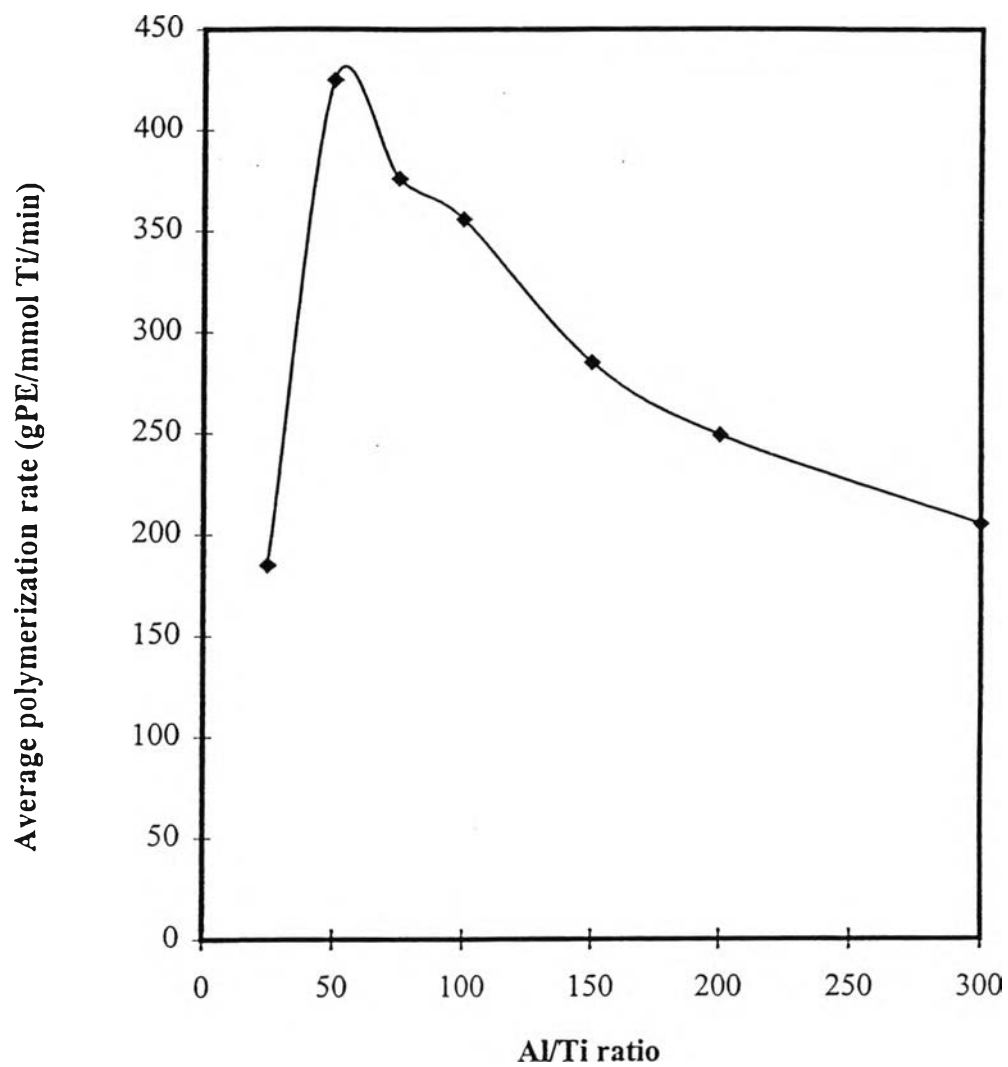


Figure 2.2 Dependence of polymerization rate on Al/Ti ratio (Chareonsuk, 1995).

Scheme 1. Equilibrium between AlEt₃ and electron donor



C* (active site)

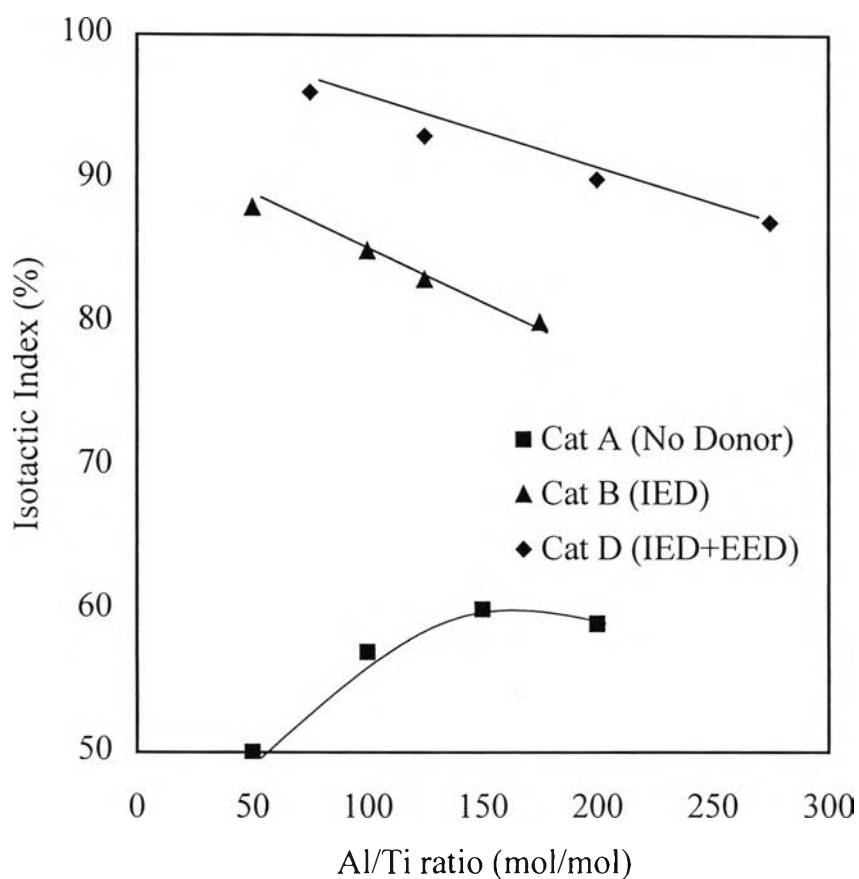
IED (internal electron donor)

EED (external electron donor)

2.3 Lewis Base

The presence of a Lewis base is needed to improve the stereospecificity of MgCl₂-supported titanium catalyst. The use of an internal Lewis base and an external Lewis base in the polymerization can give high isotacticity. Internal and external donors are commonly represented by esters of aromatic acids and alkoxy silanes. However, some works report the use of external donors that increase stereospecificity also are always accompanied with decreasing activity (Pino and Mulhaupt, 1980; Soga *et al.*, 1983; Keii *et al.*, 1983).

In the polymerization of propylene, alkoxy silanes were proven to be effective external bases (Soga *et al.*, 1988; Sacchi *et al.*, 1991). It was concluded that the silane compounds should have 2 or 3 alkoxy groups of relatively large and non-linear hydrocarbon chains in order to get high performance in term of activity and isotacticity. Xu *et al.* (1997) showed the dependence of isotactic index of polymer on Al/Ti ratio in the catalyst systems with and without electron donor (Figure 2.3).



CatalystA = $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$

CatalystB = $\text{TiCl}_4/\text{MgCl}_2/\text{di-n-butylphthalate-AlEt}_3$

CatalystC = $\text{TiCl}_4/\text{MgCl}_2/\text{di-n-butylphthalate-AlEt}_3/\text{diphenyl-dimethoxysilane}$

Figure 2.3 Dependence of isotactic index of polymer on Al/Ti ratio
(Xu *et al.*, 1997).

2.4 Mechanism

The most generally and widely accepted representation of the mechanism is related to the growth of the chain at the active center (Figure 2.4). An active center is based on a titanium atom that is in an octahedral coordination having one vacant coordination site and an adjacent coordination site bonded to an alkyl group. The mechanism involves the propagation via π -coordination of an alkene molecule by an active center at its vacant coordination site and then insertion into the titanium-alkyl bond via a four-center transition state. The growing polymer chain migrates back to its original position to maintain stereo-regular propagation steps.

However, The polymerization rate of supported Ziegler-Natta catalyst is initially high and decays rapidly to a near stationary rate. Marques *et al.* (1993) suggested that the decay in rate of polymerization could be represented by a first order decay law. In addition, Athiwattananont (1998) reported that addition of CHCl_3 or CH_2Cl_2 at an optimum ratio can retard the decay in activity.

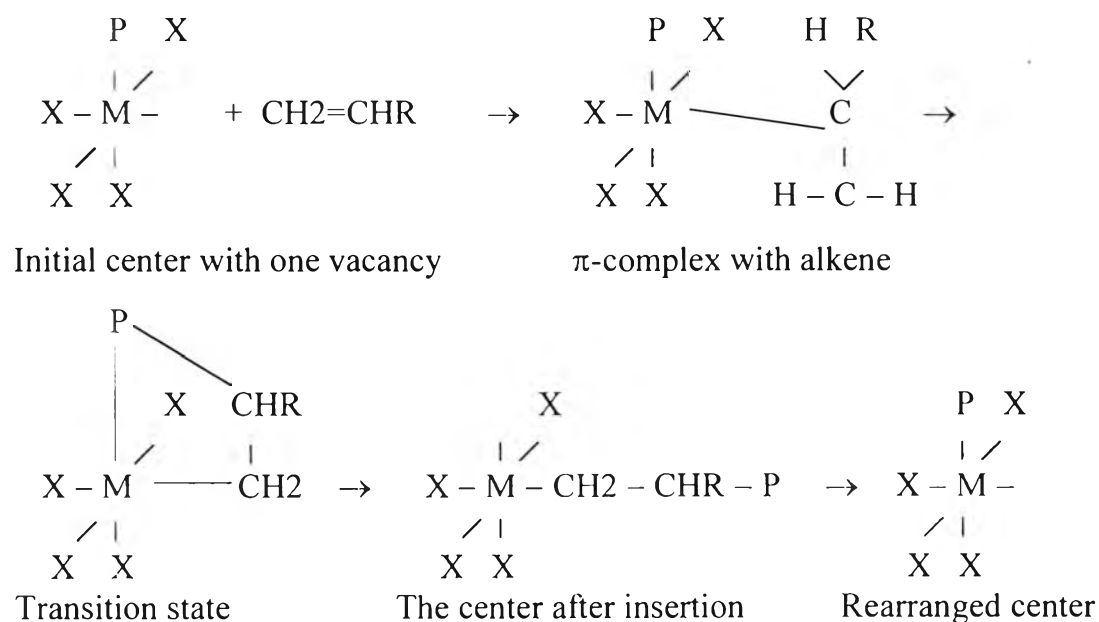


Figure 2.4 The Cossee mechanism (Cossee, 1961).