

## CHAPTER III

### LITERATURE REVIEWS

#### 3.1 Historical development of metallocene research

Metallocene-based catalysts, the so-called “single-site” catalysts have become important for the polymer industry. The evolution of the metallocene catalyst for olefin polymerization is shown in Table 3.1.

**Table 3.1.** Timetable and historical development of metallocene research<sup>[27]</sup>

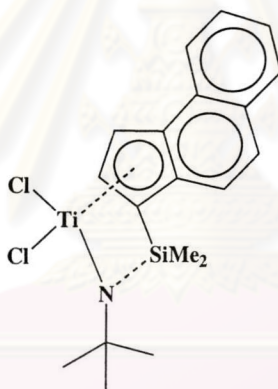
1952	Development of the structure of ferrocene (Fisher and Wilkinson)
1955	Metallocene as component of Ziegler-Natta catalysts, low activity with common aluminium alkyls
1973	Addition of small amount of water to increase the activity (Al:H <sub>2</sub> O = 1:0.05 up to 1:0.3) (Reichert, Meyer and Breslow)
1975	Unusual increase in activity by adding water at the ratio Al:H <sub>2</sub> O = 1:2 (Kaminsky, Sinn and Motweiler)
1977	Using separately prepared methylaluminoxane (MAO) as cocatalyst for olefin polymerization (Kaminsky, Sinn)
1982	Synthesis of <i>ansa</i> metallocenes with C <sub>2</sub> symmetry (Brintzinger)
1984	Polymerization of propylene using a <i>rac/meso</i> mixture of <i>ansa</i> titanocenes leading to partially isotactic polypropylene (Ewen)
1984	Chiral <i>ansa</i> zirconocene producing highly isotactic polypropylene (Kaminsky and Brintzinger)

### 3.2 Complexes from group III metals

Neutral iso-electronic group III complexes such as  $Cp_2^*MR$  ( $M = Sc, Y$  and lanthanide metals) show isolobal analogy to cationic group IV metallocenes. Highly active catalysts for the polymerization of ethylene are found in this group<sup>[33-36]</sup>. This activity is in the order  $La > Nd \gg Lu$ . These catalysts show high initial activity, but the activity decreases rapidly with time.

### 3.3 Complexes of group IV metals

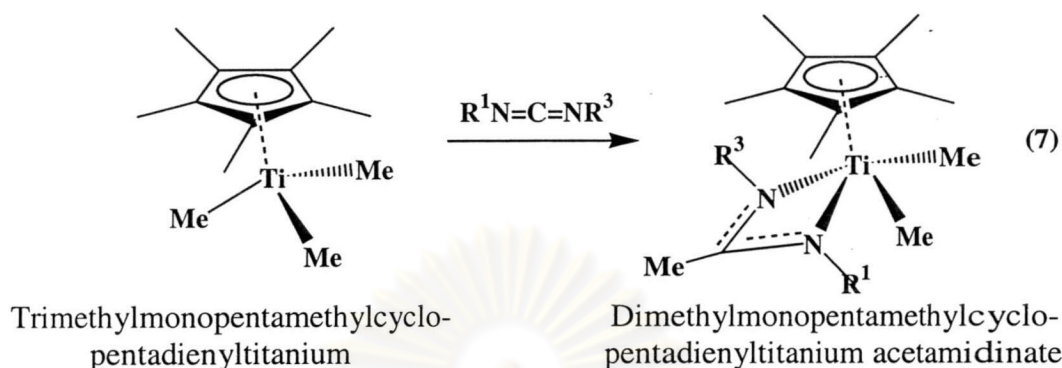
A 2-methylbenz(e)indenyl-based *ansa*-monocyclopentadienylamido titanium catalyst was reported<sup>[37]</sup>. This catalyst was used to copolymerize ethylene and 1-octene and gave high activities and good 1-octene inclusion, high molecular weight ( $M_w = 327,000$  and  $MWD = 1.8$ ):



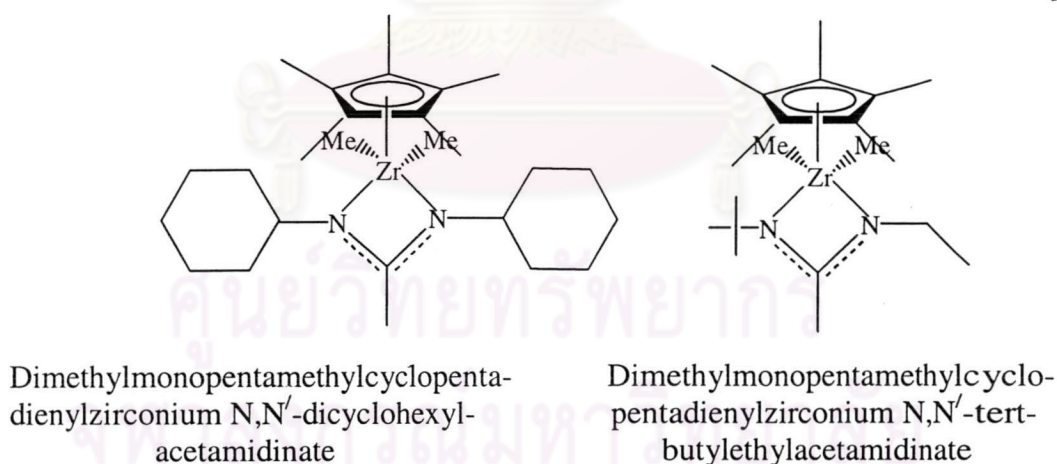
**Dimethylsilyl-2-methylbenz[e]indenyl-N-tert-butylamidotitaniumdichloride**

Schaffer *et al.*<sup>[38]</sup> reported the copolymerization of ethylene and isobutylene with metallocene catalysts. Previously  $Et(Ind)_2ZrCl_2/MAO$  had been used to copolymerize ethylene and isobutylene, but the isobutylene incorporation was very low. The incorporation of isobutylene was claimed up to levels of 45%. The catalyst used was  $Me_2Si(Cp^*)cyclodecylamidodimethyl$  titanium, activated by either dimethylaniliniumtetrakis(pentafluorophenyl)borate, triphenylmethyltetrakis(pentafluorophenyl)borate or MAO. The cocatalysts were chosen to prevent any possible carbocationic polymerization of isobutylene. Activities of  $100,000$  to  $400,000 \text{ g mol}^{-1} \text{ h}^{-1}$  were reported (very similar to those for ethylene/styrene polymerization) and molecular weights varied between  $9,000$  and  $50,000 \text{ g/mol}$ .

Sita *et al.*<sup>[39]</sup> described the synthesis of a wide range of derivatives of  $\text{Cp}^*\text{TiMe}_2\text{-}[\text{NR}^1\text{-C(Me)NR}^3]$  in high yield and used them for the polymerization of ethylene upon activation by MAO.

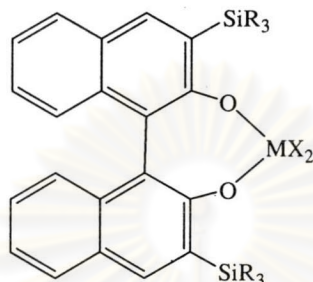


Jayaratne *et al.*<sup>[40]</sup> found that a class of dimethyl - monocyclopentadienyl zirconium acetamidinates,  $\text{Cp}^*\text{ZrMe}_2[\text{NR}^1\text{C}(\text{Me})\text{NR}^2]$  ( $\text{R}^1 = t\text{-Bu}$ ,  $\text{R}^2 = \text{cyclohexyl}$  or 2,6-diisopropylphenyl) was catalyst precursors for the living Ziegler-Natta polymerization of  $\alpha$ -olefin upon activation by a borate cocatalyst. The stereo-specific living polymerization of 1-hexene has been achieved to provide highly isotactic, high molecular weight (11,000 – 69,500) materials possessing low polydispersities (1.0 – 1.5).



Schaverien *et al.*<sup>[29]</sup> prepared the titanium or zirconium sterically hindered chelating alkoxide complexes  $\{1, 1'-(2, 2', 3, 3'\text{-OC}_{10}\text{H}_5\text{SiR}_3)\}_2\text{ZrCl}_2$  ( $\text{R}_3 = \text{Me}_3$  (1),  $\text{MePh}_2$  (2),  $\text{Ph}_3$  (3)) by reaction of  $\text{M}(\text{CH}_2\text{Ph})_4$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) or  $\text{Zr}(\text{CH}_2\text{Ph})_2\text{Cl}_2(\text{OEt}_2)_2$  with the appropriate biphenol or binaphthol, or by reaction of  $\text{TiCl}_4$  with the diol. The chelating phenoxide and binaphthoxide titanium and zirconium species, in the presence of an aluminum cocatalyst are active for the oligo-polymerization of  $\alpha$ -

olefins. Steric modifications also have a clear influence on the degree of 1-hexene polymerization as well as the tacticity of poly(1-hexene). In particular, the chelating alkoxide ligand framework can induce stereoregularity. For **1** and **2**, with methylaluminoxane as cocatalyst (100 equiv.), regioregular and stereospecific polymerization of 1-hexene is observed to give high molecular weight ( $M_w = 674,000$ ,  $M_w/M_n = 2.2$ ) and highly (> 90%) isotactic polyhexene.



3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthoxido-titanium or zirconium dihalide complex

Deelman *et al.*<sup>[41]</sup> synthesized the mono(1-azaallyl)zirconium complexes,  $Zr\{N(SiMe_3)C(R^1)C(R^2)(C_5H_4N-2)\}Cl_3$  ( $R^1 = Ph$ ,  $R^2 = SiMe_3$  (**1d**);  $R^1 = t-Bu$ ,  $R^2 = H$  (**2d**)) and  $Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_9H_6N-2)\}Cl_3$  (**3d**). When activated with MAO, these compounds were highly active in ethylene polymerization. Compound **1d** also showed some oligomerization of 1-hexene (activity =  $0.133 \text{ g mol}^{-1}\text{h}^{-1}$ ) and the copolymerization of ethylene and 1-hexene (activity =  $2,700 \text{ g mol}^{-1}\text{h}^{-1}$ ).

Using the disymmetric  $N,N'$ -bis(trimethylsilyl)aminobenzylamine ( $H_2MABA$ ; **1**) ligand, the new group 4 metal complexes  $(MABA)TiCl_2$  (**2**),  $(MABA)TiMe_2$  (**3**),  $(MABA)Ti(CH_2Ph)_2$  (**4**),  $(MABA)ZrCl_2$  (**5**), and  $(MABA)Zr$  (**6**) were prepared.<sup>[42]</sup> Complexes **2** and **4** activated by MMAO (1000 equiv) and  $B(C_6F_5)_3$  respectively, have moderate catalytic activities for the polymerization of 1-hexene (activity = 9,200 and 92,500  $\text{g mol}^{-1} \text{h}^{-1}$ ,  $M_w = 6,990$  and 56,600,  $M_w/M_n = 3.2$  and 5.1 respectively).



**M = Ti, Zr**  
**R = Cl, Me, CH<sub>2</sub>Ph**

$N,N'$ -bis(trimethylsilyl)aminobenzyltitaniumdialkyl complex

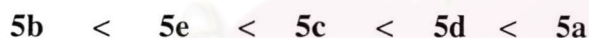
Shiono *et al.*<sup>[43]</sup> polymerized propylene and 1-hexene with the conventional  $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  catalyst in the presence of  $\text{Zn}(\text{C}_2\text{H}_5)_2$  as chain transfer reagent. The catalyst produces isotactic polyolefins as well as olefin copolymers. In addition,  $\text{Zn}(\text{C}_2\text{H}_5)_2$  reduces the molecular weight of polymers. The  $\text{TiCl}_3/\text{Zn}(\text{C}_2\text{H}_5)_2$  catalyst system was found to be active for the 1-hexene polymerization even in the absence of  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ . The activity of  $\text{TiCl}_3/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  was about 10 times higher than that of the  $\text{TiCl}_3/\text{Zn}(\text{C}_2\text{H}_5)_2$  system.

Nomura *et al.*<sup>[44]</sup> studied the effect of substituent on cyclopentadienyl group for catalytic activity in 1-hexene and 1-octene polymerization with the series of  $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  [ $\text{Cp}' = \text{Cp}$  (**1a**), *t*- $\text{BuC}_5\text{H}_4$  (**2a**), 1,3- $\text{Me}_2\text{C}_5\text{H}_3$  (**3a**), 1,3-*t*- $\text{BuC}_5\text{H}_3$  (**4a**), and  $\text{C}_5\text{Me}_5$  (**5a**)]-methylaluminoxane (MAO) catalysts have been explored, and the activity increased in the order:



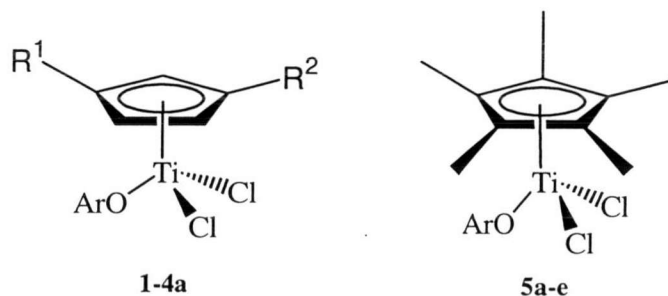
$$(26,000) \quad (63,000) \quad (89,000) \quad (184,000) \quad (728,000) \text{ g mol}^{-1}\text{h}^{-1}$$

The catalytic activity in 1-hexene polymerization with the series of  $\text{Cp}^*\text{TiCl}_2(\text{OAr})$  [ $\text{OAr} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$  (**5a**), 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$  (**5b**), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$  (**5c**), 2-*t*- $\text{Bu}-4,6\text{-Me}_2\text{C}_6\text{H}_2$  (**5d**), 4- $\text{MeC}_6\text{H}_4$  (**5e**)]-MAO catalysts increased in the order:

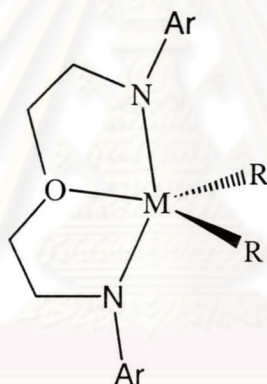


$$(39,000) \quad (48,000) \quad (76,000) \quad (694,000) \quad (728,000) \text{ g mol}^{-1}\text{h}^{-1}$$

Although (1,3-*t*- $\text{BuC}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**4a**) showed the lowest catalytic activity for polymerization of both 1-hexene and 1-octene, **4a** exhibited the significant activity for copolymerization of ethylene with 1-hexene, resulting in obtaining copolymer with relatively high 1-hexene contents (20.2-36.5 mol%) with relatively narrow molecular weight distributions.

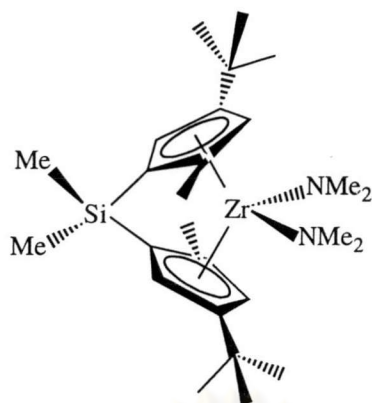


Group 4 complexes (Ti, Zr, Hf); [**1a**, **1b**]TiCl<sub>2</sub>, [**1a**, **1b**]TiMe<sub>2</sub>, [**1a**]Ti(CH<sub>2</sub>Ph)<sub>2</sub>, [**1a-c**]M(NMe<sub>2</sub>)<sub>2</sub> (M = Zr or Hf), [**1a-1c**]MCl<sub>2</sub> and [**1a-1c**]MR<sub>2</sub> (**1a** = (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, **1b** = (2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, **1c** = (2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O and R = Me, Et, <sup>i</sup>-Bu) were prepared by Aizenberg *et al.*<sup>[45]</sup> Addition of 1 equivalent of [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>D<sub>5</sub>X (X = Br, Cl) to [**1a**, **c**]MMe<sub>2</sub> (M = Zr, Hf) gave cationic complexes that contain coordinated dimethylaniline. Analogous cations can be prepared in the sulfur ligand system. Zr and Hf dimethyl complexes that contain an oxygen donor or a sulfur donor ligand can be activated with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to yield efficient catalysts for polymerization of 1-hexene, although the molecular weight of the poly(1-hexene) chains is limited to ~20,000~25,000 under the conditions employed. Neither {[**1c**]ZrMe(ether)} [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] nor {[**1c**]HfMe(ether)} [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] polymerized 1-hexene in C<sub>6</sub>D<sub>5</sub>Br at room temperature.



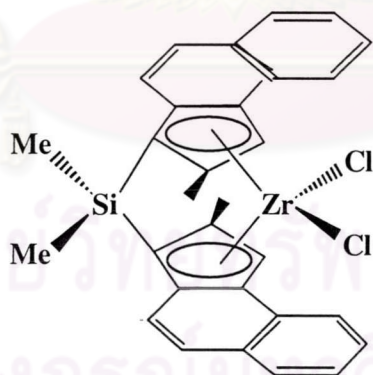
Chelating tridentate diamido/O donor metal Group 4 complex

Polymerizations of higher  $\alpha$ -olefins, 1-pentene, 1-hexene, 1-octene and 1-decene were carried out at 30°C in toluene by using highly isospecific *rac*-Me<sub>2</sub>Si(1-C<sub>5</sub>H<sub>2</sub>-2-CH<sub>3</sub>-4-<sup>i</sup>Bu)<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> compound in the presence of Al(*i*Bu)<sub>3</sub>/[CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as cocatalyst<sup>[46]</sup>. Highly isotactic poly( $\alpha$ -olefin)s of high molecular weight (M<sub>w</sub>) were produced. The M<sub>w</sub> decreased from polypropylene to poly(1-hexene), and then increased from poly(1-hexene) to poly(1-decene). The isotacticity of the polymer decreased in the order: poly(1-pentene) > poly(1-hexene) > poly(1-octene) > poly(1-decene).



Dimethylsilylbis(3-tert-butyl-5-methyl)cyclopentadienylzirconium  
diN,N'-dimethyl

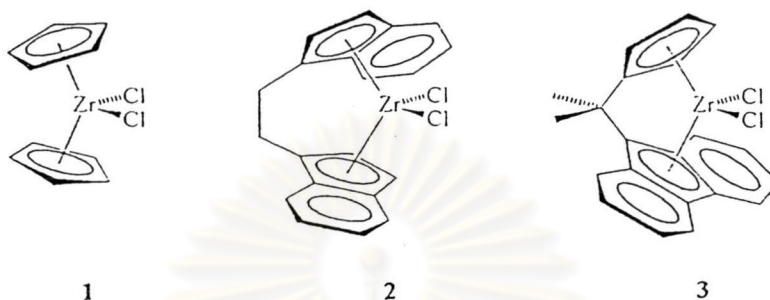
Brull *et al.*<sup>[47]</sup> synthesized poly( $\alpha$ -olefins) ranging from poly(1-pentene) to poly(1-octadecene) with narrow MWD (2.1-3.7) by using  $(\text{CH}_3)_2\text{Si}(2\text{-methylbenz[e]indanyl})_2\text{ZrCl}_2$  and methylaluminoxane at polymerization temperature ranging from  $-15^\circ\text{C}$  to  $180^\circ\text{C}$ . The molecular weight of the obtained polymers increases with decreasing polymerization temperature. At polymerization temperature ranging from  $20$  to  $100^\circ\text{C}$ , moderate isotacticity prevailed, but outside this temperature range, the polymer was less stereoregular.



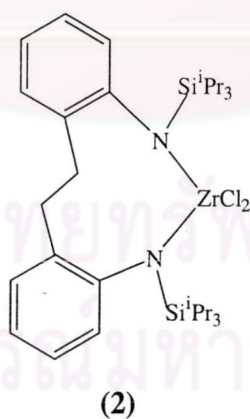
Dimethylsilylbis2-methylbenz[e]indenylzirconium dichloride

Frauenrath *et al.*<sup>[48]</sup> used catalyst systems consisting of different zirconocene dichlorides [ $\text{CpZrCl}_2$ (**1**),  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (**2**) and  $^i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ (**3**)] and MAO as the cocatalyst for 1-hexene polymerization. The polymerization behaviour of 1-hexene has been studied as a function of polymerization temperature ( $\text{Al/Zr} = 5,000$ ,  $[\text{Zr}] = 1 \times 10^{-4} \text{ M}$ ). The molecular weight distributions of poly(1-hexene)s obtained with (**1**) at

temperatures between 0°C and -60°C are bimodal. Proceeding from high to low temperatures, a high molecular weight shoulder develops at  $T_p = 0^\circ\text{C}$ , which increases with decreasing temperatures. The same is observed for polymerizations with (2) and (3) produces lower molecular weight poly(1-hexene)s than the other catalysts.



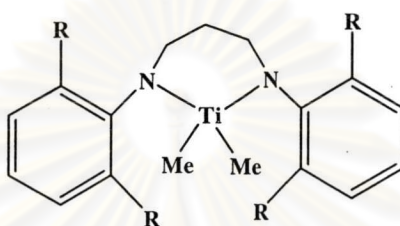
Jeon *et al.*<sup>[49]</sup> prepared the new ancillary ligand 2,2'-ethylenebis(*N,N'*-(triisopropylsilyl)anilino) (*EBT<sup>t</sup>P*, 1), the zirconium complexes (*EBT<sup>t</sup>P*)ZrCl<sub>2</sub> (2) and (*EBT<sup>t</sup>P*)ZrMe<sub>2</sub> (3). Complex 2, activated by MAO, and complex 3, activated by either MAO (500 equiv) or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, are good catalysts for the polymerization of terminal olefins. The polymerization of 1-hexene catalyzed by 3/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at low temperature (0°C) is living (activity = 540,000 and 394,000 g mol<sup>-1</sup>h<sup>-1</sup>, Mw = 26,517 and 146,088 and MWD = 1.2).



Scollard *et al.*<sup>[50]</sup> studied the reaction of RHN(CH<sub>2</sub>)<sub>3</sub>NHR (1a, b) (a, R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; b, R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with 2 equiv of BuLi, following by 2 equiv of ClSiMe<sub>3</sub> yields the silylated diamines R(Me<sub>3</sub>Si)N(CH<sub>2</sub>)<sub>3</sub>N(SiMe<sub>3</sub>)R (3a, b). The reaction of 3a, b with TiCl<sub>4</sub> yields the dichloride complexes [RN(CH<sub>2</sub>)<sub>3</sub>NR]TiCl<sub>2</sub> (4a, b) and two equiv of ClSiMe<sub>3</sub>. Compounds 4a, b react with 2 equiv of MeMgBr to



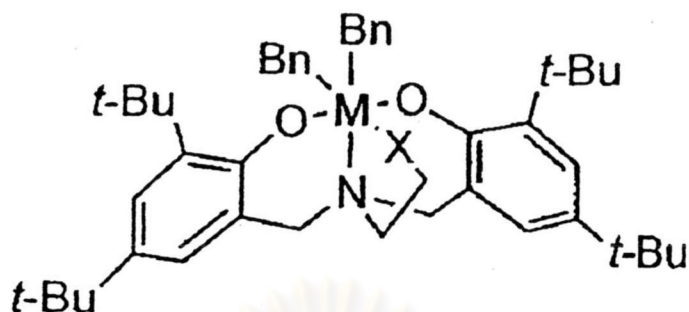
give the dimethyl derivatives  $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{TiMe}_2$  (**5a**, **b**). These titanium dimethyl complexes are active catalysts for the polymerization of 1-hexene, when activated with methylaluminoxane (MAO). Activities up to  $350,000,000 \text{ g mol}^{-1}\text{h}^{-1}$  were obtained in neat 1-hexene. These systems actively engage in chain transfer to aluminum. Equimolar amounts of **5a** or **5b** and  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyze the living aspecific polymerization 1-hexene. MWDs as low as 1.0 were measured. Highly active living systems are obtained when **5a** is activated with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .



1,3-Di(2,6-dialkylphenyl)amidopropanetitanium dimethyl

Nomura *et al.*<sup>[51]</sup> prepared various titanium (IV) complexes of type  $\text{Cp}'\text{Ti}(\text{OAr})\text{Cl}_2$  and  $\text{Cp}^*\text{Ti}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Me}_2$  ( $\text{Cp}'$  = cyclopentadienyl;  $\text{OAr}$  = aryloxy ;  $\text{Cp}^*$  =  $\text{C}_5\text{Me}_5$ ). These complexes were activated by using MAO or  $\text{Al}^i\text{Bu}_3\text{-Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  cocatalyst giving  $\text{Cp}^*\text{Ti}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{X}_2$  [  $\text{X} = \text{Cl}$  (**2b**),  $\text{Me}$  (**8b**),  $\text{CF}_3\text{SO}_3$  (**9b**)]. Complex **2b** was found to be an effective catalyst precursor for 1-hexene polymerization by working with MAO cocatalyst.

Tshuva *et al.*<sup>[52]</sup> studied several  $[\text{ONXO}]$ -type zirconium and hafnium dibenzyl complexes of amine bis(phenolate)ligand, where X is a heteroatom donor located on a pendant arm ( $\text{X} = \text{N}, \text{O}, \text{S}$ ). These complexes were synthesized directly from the ligand precursors and the corresponding tetrabenzyl metal complexes in quantitative yields. All complexes exhibited remarkable activities in the polymerization of 1-hexene using  $\text{B}(\text{C}_6\text{F}_5)_3$  as cocatalyst, yielding high molecular weight polymers ( $M_w$  is in range 20,000-250,000). The activity order of the zirconium complexes as a function of the side-arm donor was found to be  $\text{OMe} > \text{NMe}_2 > \text{SMe}$  (5:2:1). However, the activity order was found to be different in the hafnium series, namely  $\text{SMe} > \text{OMe} > \text{NMe}_2$  (3.5:1.5:0.2), the  $[\text{ONSO}]$ -type complex exhibiting the highest activity ever reported for a hafnium complex under the conditions employed.



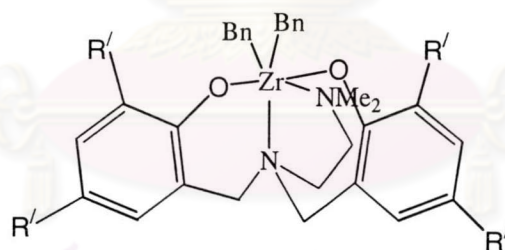
Chelating tetradentate [ONXO]-type Goup 4 metal dibenzyl complex of amine bis(phenolate) ligand (X = NO,S)

Nomura *et al.*<sup>[53]</sup> studied the effect of cocatalyst in 1-hexene polymerization by using  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$  catalyst and reported that  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$  (**2**) exhibited higher initial catalytic activity than  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$  (**1**) for 1-hexene polymerization in the presence of MAO, the effect of cocatalyst for the polymerization was investigated at low temperature (0 - 30°C). The use of  $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  was found to be effective to improve the activity and a notable increase in the activity was obtained if **2** was pre-treated with 2 equivalent of  $\text{Al}^i\text{Bu}_3$  in advance. Activity of 5,710,000  $\text{g mol}^{-1}\text{h}^{-1}$  could be attained after 16 min under the optimized conditions and the  $M_n$  value for the resultant poly(1-hexene) increased upon the consumption of 1-hexene suggesting the possibility of living polymerization.

Flores *et al.*<sup>[54]</sup> studied the preparation of diamido O-donor ligand; *cis*-2,5-( $\text{Ar}'\text{NHCH}_2$ )<sub>2</sub>( $\text{C}_4\text{H}_6\text{O}$ ) ( $\text{H}_2$ [**1**]) and *cis*-2,5-( $\text{Ar}'\text{NHCH}_2$ )( $\text{Ar}\text{NHCH}_2$ )( $\text{C}_4\text{H}_6\text{O}$ ) ( $\text{H}_2$ [**2**];  $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ). The reaction between  $\text{Zr}(\text{NMe}_2)_4$  and  $\text{H}_2$ [**1**] yielded [**1**]Zr(NMe<sub>2</sub>)<sub>2</sub>, from which [**1**]ZrCl<sub>2</sub> and [**1**]ZrMe<sub>2</sub> were prepared readily. The stable cations of the type {[**1**]ZrMe(PhNMe<sub>2</sub>)}[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and {[**2**]ZrMe(PhNMe<sub>2</sub>)} [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], prepared in the reaction between the dimethyl species and [PhNHMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], could be observed, while cations prepared in the reaction between the dimethyl species and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] appeared to be relatively unstable. Poly(1-hexene) that had a molecular weight approximately 45000 could be prepared by employing [**1**]ZrMe<sub>2</sub> activated with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene at 0°C.

Warren *et al.*<sup>[55]</sup> prepared (CyBen)M(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> complexes (CyBen)<sup>2-</sup> = [(cyclohexyl)<sub>2</sub>BNCH<sub>2</sub>CH<sub>2</sub>NB(cyclohexyl)<sub>2</sub>]<sup>2-</sup> by the reaction between Li<sub>2</sub>(CyBen) (ether) and M(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(ether)<sub>x</sub> (M = Ti, Zr, or Hf). Diisobutyl complex (CyBen)Zr(CH<sub>2</sub>CHMe<sub>2</sub>)<sub>2</sub> reacts with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene at -30°C to give the cation (CyBen)Zr(CH<sub>2</sub>CHMe<sub>2</sub>) [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], which is believed to be stabilized by coordination of chlorobenzene or toluene. Chlorobenzene solutions of (CyBen)M (CH<sub>2</sub>CHMe<sub>2</sub>)(S) [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (M = Zr, Hf; S = chlorobenzene) polymerize 225 equiv of 1-hexene quantitatively at -30°C to give regioregular poly(1-hexene) of high molecular weight ( $M_n = (0.4-1.3) \times 10^5$  g/mol) and high polydispersity (5-6).

Tshuva *et al.*<sup>[56]</sup> synthesized diamine bis(phenolate) [ONNO]<sup>-</sup> ligands by a one-pot Mannich condensation between N,N'-dimethyl-ethylenediamine, 2 equiv of formaldehyde and 2 equiv of substituted phenol {2,4-di-*tert*-butyl-phenol (**1**) and 2,4-di-methyl-phenol (**2**)}. Upon reaction with tetra(benzyl)zirconium, zirconium complexes; [ONNO]ZrBn<sub>2</sub> (**1a**) and (**2a**) were afforded. Upon activation with tris (pentafluorophenyl)borane, **1a** was found to be an active 1-hexene polymerization catalyst (activity of 18,000 g mol<sup>-1</sup> h<sup>-1</sup>). The isotactic poly(1-hexene) obtained had a molecular weight Mw of 12,000 and a narrow MWD (1.15).

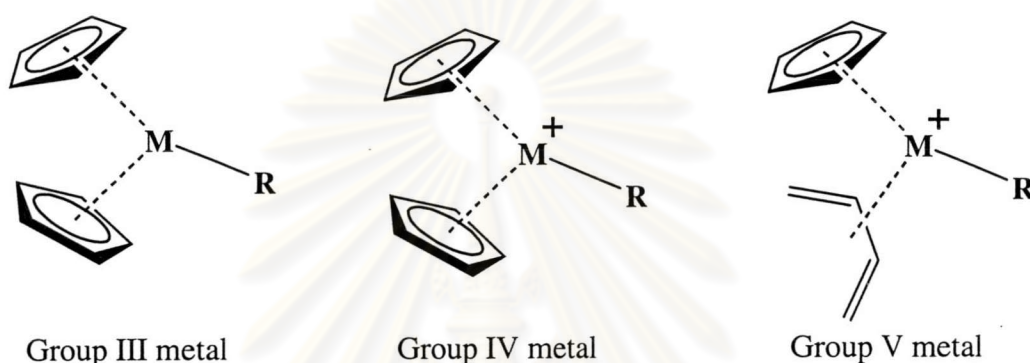


**1a and 2a**

Baumann *et al.*<sup>[57]</sup> studied a variety of five- and six-coordinate titanium and zirconium dialkyl complexes that contain the [(*i*-PrN-*o*-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O]<sup>2-</sup> ([*i*-PrNON]<sup>2-</sup>) ligand: [*i*-PrNON]Ti(CH<sub>2</sub>CHMe<sub>2</sub>)<sub>2</sub>, [*i*-PrNON]Ti(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>, [*i*-PrNON]Zr(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, and [*i*-PrNON]Zr(CH<sub>2</sub>CHMe<sub>2</sub>)<sub>2</sub> and analogous dialkyl complexes [CyNON]MR<sub>2</sub> (Cy = cyclohexyl; M = Zr, R = Me, Et, *i*-Bu, CH<sub>2</sub>CMe<sub>3</sub>, allyl; M = Ti, R = Me, CH<sub>2</sub>CMe<sub>3</sub>, *i*-Bu). Consistent with the relatively uncrowded coordination sphere in [*i*-PrNON]<sup>2-</sup> or [CyNON]<sup>2-</sup> complexes, activated dialkyls will only oligomerize 1-hexene.

### 3.4 Complexes of group V metals

Whereas the complexes  $\text{NbCl}_3\text{Cp}_2$ ,  $\text{NbCl}_2\text{Cp}_2$  and  $\text{NbCl}_4\text{Cp}$  show no polymerization activity, the types of complex  $[\text{MRCp}(1,3 \text{ diene})]^+$  where  $\text{M} = \text{Nb}$  and  $\text{Ta}$  were found to give “living” polymerization of ethylene<sup>[58]</sup>. Similar substituted Cp-based catalysts polymerized ethylene to  $M_n = 23,000$  and  $MWD = 1.05$  at  $T_p = -20^\circ\text{C}$ , while the same polymerization at  $T_p = 20^\circ\text{C}$  gives PE with  $M_n = 83,000$  and  $MWD = 1.3$ .<sup>[59]</sup>



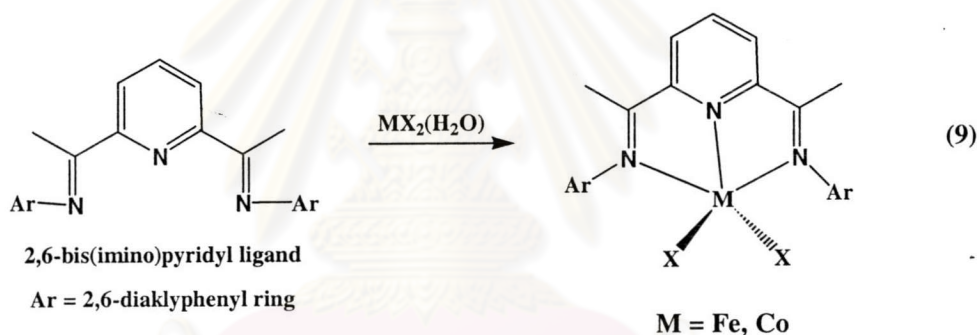
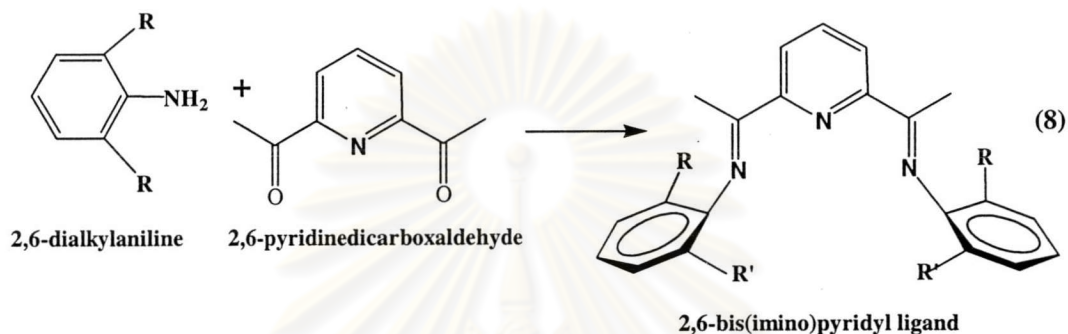
### 3.5 Complexes of group VI metals

Organochromium complexes are able to polymerize ethylene.<sup>[58,60]</sup> The complex  $[\text{Cp}^*\text{CrMe}(\text{THF})_2]^+(\text{PPh}_4)^-$  shows very low activity, but the isoelectronic analogue  $(\text{RN})_2\text{CrX}_2$  with  $\text{R} = t\text{-Bu}$  or  $\text{Ph}$ ,  $\text{X} = \text{CH}_2\text{Ph}$ ,  $\text{Cl}$  are active for ethylene polymerization. Tris(butadiene) complexes of  $\text{Mo}$  and  $\text{W}(0)$  also show activity for the polymerization of ethylene.

### 3.6 Complexes of group VIII-X metals

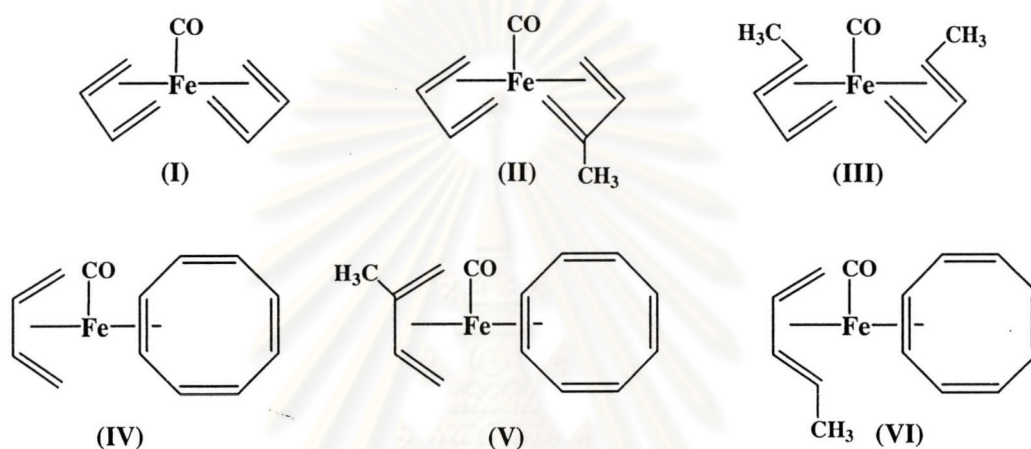
The metals of group VIII-X tend to catalyse the dimerization and oligomerization of the olefins, they prefer  $\beta$ -hydrogen elimination followed by reductive elimination. There are however some exceptions, in particular complexes of  $\text{Pd}$  and  $\text{Ni}$ . Ni-diimine complexes were reported to give the living polymerization of ethylene and  $\alpha$ -olefins.

New catalyst systems by Brookhart *et al.*<sup>[13]</sup>, iron(II) and cobalt(II) catalysts are based on tridentate pyridine bisimine ligands, in which the imine moieties are bulky ortho-substituted aryl rings. The key to the polymerization activity of these late transition metal catalysts are the bulky ortho substituents on the aryl group in the catalyst systems. The catalyst preparation and structures are presented below:



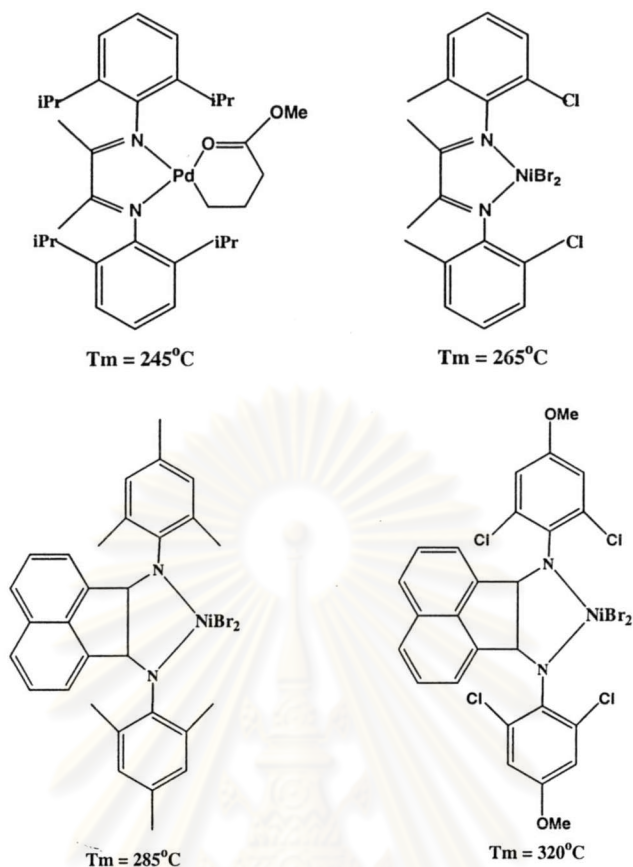
Ballivet *et al.*<sup>[61]</sup> reported a preparation of the catalytic species by two methods. In method (a)  $[Fe(NO)_2Cl]_2$  is mixed with  $AgPF_6$ ,  $AgBF_4$ ,  $AgClO_4$  or  $NaBPh_4$  and the pure on dilute substrate added. In method (b) the compound  $[Fe(NO)_2L_n]Y$  (L = acetonitrile, acrylonitrile, triphenylphosphine; Y =  $PF_6$ ,  $BF_4$ ,  $ClO_4$ ,  $BPh_4$ ) is formed before the addition of the reacting olefin. Acrylonitrile is polymerized by type (a) and (b) catalysts (L = MeCN). The compound  $[Fe(NO)_2L_n]BPh_4$  is inactive when L is triphenylphosphine. Styrene is polymerized at low temperature ( $-20^\circ C$ ) by using type (a) catalyst and polar medium. Finally, norbornadiene is dimerized selectively to the exo-trans-exo dimer (95%). The starting material  $[Fe(NO)_2Cl]_2$  (type (a) catalyst) is active whereas  $[Fe(NO)_2(MeCN)_n]PF_6$  is not.

Carbonaro *et al.*<sup>[62]</sup> prepared dibutadienecarbonyliron (I), diisoprenecarbonyl iron (II), di-1,3-pentadienecarbonyliron (III), isoprenecyclooctatetraenecarbonyliron (V) and 1,3-pentadienecyclooctatetraenecarbonyliron (IV) complexes. All compounds smoothly oligomerized butadiene. In the presence of protic acids (HCl, CCl<sub>3</sub>COOH), (I), (II), and (III) readily induce butadiene polymerization at -10°C and 0°C, whereas (IV), (V) and (VI) are transformed into stable allylic derivatives. Molecular weight (Mw) of the obtained polybutadiene is 4700.

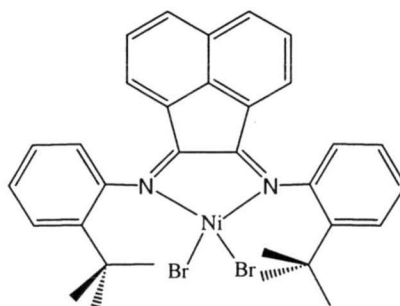


Zhang *et al.*<sup>[63]</sup> studied the polymerization of butadiene that catalyzed by Fe<sup>-</sup>(acac)<sub>3</sub>-Al(i-Bu)<sub>3</sub>-phenanthroline catalyst. A suitable composition for the catalyst was determined; Ph/Fe > 0.2, Fe/Bu = 1 × 10<sup>-4</sup>, Al/Fe ≥ 20. The polymer obtained with such a catalyst consists of equal amounts of cis-1,4-polybutadiene and 1,2-polybutadiene. The polymerization temperature is raised, the conversion of butadiene decreases, accompanied by a decrease in intrinsic viscosity and 1,2-contents as well as an increase in trans-1,4-content.

Additionally, Brookhart *et al.*<sup>[61]</sup> have reported on the use of Ni(II) and Pd(II) catalysts for the polymerization of cyclopentene. Unlike the case when cyclopentene is polymerized with C<sub>2</sub>-symmetric metallocenes and highly crystalline materials with T<sub>m</sub> = 395°C is obtained, the Ni and Pd catalysts below give lower melting temperatures, probably due to lower tacticities of the polymers.



Peruch *et al.*<sup>[62]</sup> studied the elementary reactions involved in the catalytic activation process of  $\alpha$ -diimine  $\text{NiBr}_2$  by methylaluminoxane (MAO) for 1-hexene polymerization kinetics, UV-visible spectroscopic analysis of the catalytic system and structural analysis of the poly(1-hexene) formed. Spectroscopic data have underlined the important role of the monomer in the stabilization process of the nickel-based active species. Partial polymerization orders with respect to MAO, nickel derivative and monomer were determined. An apparently negative monomer order of the polymerization corresponding to a decrease of the polymerization rate with an increase of monomer concentration in the reacting medium was observed.



Chelating diimine nickel dibromide complex