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Kohtaro Osakada *Editor*

Organometallic Reactions and Polymerization

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Kohtaro Osakada
Editor

Organometallic Reactions and Polymerization

Springer

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Preface

Olefin polymerization using transition-metal catalysts has revolutionized materials science and petroleum industry, and created an affluent society worldwide. Thus, the discovery of ethylene polymerization under low pressure using Ziegler-Natta catalysts should be ranked among the most important discoveries of the past century. Research on a homogeneous version of olefin polymerization catalysts, represented by metallocene catalysts, took off in the 1980s, which resulted in additional progress in polymer science and technology as well as in related research fields. The catalysts composed of transition metal complexes have enabled controlled synthesis of a number of polyolefins and olefin copolymers with the proper choice of an auxiliary ligand for the molecular transition-metal complex. The structures of the above-mentioned molecular catalysts can be easily modified, which improves the reactivity and selectivity of olefin polymerization. Another important achievement in the use of molecular transition metal complexes as catalysts is the elucidation of the reaction mechanism of olefin polymerization. The exact reaction pathways and detailed account of the stereocontrol of such polymerization can be discussed on the basis of the catalyst structure and polymerization results. Organotransition-metal chemistry has developed together with coordination polymerization because its fundamental reactions, including the migratory insertion and β-hydrogen elimination of olefins, play key roles in polymerization catalyzed by transition-metal complexes. Progress in research on coordination polymerization continues to generate new polymer materials from olefins that are economically and environmentally favorable.

This issue of Lecture Note Series contains eight articles covering the polymerization using various organotransition-metal catalysts, including early- and late- transition-metal complexes, new trends in olefin oligomerization, and related reactions. All the authors have ensured that their article includes the historical and scientific backgrounds of the field, current research progress, and further scope of research. The whole book is designed to deliver eight independent lectures from the authors. Since the authors involved are well versed in organometallic chemistry, the discussion in each chapter is based on a profound understanding of the reactions and structures of organotransition-metal complexes. A few topics overlap among the chapters so that the readers may choose to start reading particular chapters in the book first. We included two final chapters on olefin metathesis and cross-coupling polymerization. These two reactions are composed of fundamental reactions of organotransition-metal complexes, similar to the coordination polymerization, and at present have become crucial materials science and device technology.

The project of publishing this book in its present form started with an invitation from Springer Publishing to contribute to the series “Lecture Notes in Chemistry”. We would like to acknowledge the initiative of Dr. Tien-Yau Luh, editor of the series of books, and the kind cooperation of Elizabeth Hawkins in bringing this book to fruition.

Kohtaro Osakada

Contents

1 Olefin Polymerization with Metallocene Catalysts 1

Takeshi Shiono

1.1 Introduction 1

1.2 Elementary Processes of Olefin Polymerization. 3

1.2.1 Initiation and Propagation Reactions 3

1.2.2 Chain Transfer and Termination Reaction 3

1.2.3 Molecular Weight and Molecular Weight Distribution. . . 5

1.3 Structure of Vinyl Polymer and Stereospecific Polymerization 8

1.3.1 Stereoregularity of Vinyl Polymer. 8

1.3.2 Regiochemistry in Propylene Polymerization 8

1.3.3 Origin of Stereospecificity 10

1.3.4 Polymerization Mechanism and Microtacticity 11

1.4 Copolymer and Copolymerization 16

1.4.1 Structure of Copolymers 16

1.4.2 Copolymerization 16

1.5 Characteristics of Metallocene Catalysts. 27

1.5.1 Activation Process of Metallocene 27

1.5.2 Tacticity Control of Polypropylene 31

1.5.3 Control of Chain Transfer Reaction. 39

1.5.4 Copolymerization of Olefins. 41

1.6 Conclusion 46

References 47

2 Olefin Polymerization with Half-Metallocene Catalysts 51

Kotohiro Nomura and Jingyu Liu

2.1 Introduction 51

2.2 Modified Half-Titanocenes as Olefin Polymerization Catalysts. 52

2.2.1 Olefin Polymerization by Half-Titanocenes Containing Aryloxo Ligands. 54

2.2.2 Selected Examples in Olefin Polymerization by Half-Titanocenes Containing the Other Anionic Ancillary Donor Ligands 56

2.2.3 Copolymerizations of Ethylene with Sterically Encumbered α-olefins 59
2.2.4 Copolymerization with Cyclic Olefins 67
2.3 Syndiospecific Styrene Polymerization and Ethylene/Styrene Copolymerization Using Half-Titanocenes: Ligand Effects and Some New Mechanistic Aspects 70
2.3.1 Syndiospecific Styrene Polymerization Using Cp'TiX_2(Y)–MAO Catalyst Systems 71
2.3.2 Ethylene/Styrene Copolymerization Using Half-Titanocenes. 73
2.3.3 Role of Anionic Donor Ligand in Ethylene/Styrene Copolymerization and Syndiospecific Styrene Polymerization: Mechanistic Considerations. 79
2.4 Summary and Outlook 81
References 82

3 Olefin Polymerization with Non-metallocene Catalysts (Early Transition Metals) 89
Kotohiro Nomura and Wenjuan Zhang
3.1 Introduction 89
3.2 Design, Synthesis of Molecular Catalyst with Early Transition Metals. 90
3.2.1 Titanium, Zirconium, and Hafnium Complexes. 90
3.2.2 Vanadium Complexes 98
3.2.3 Miscellaneous Early Transition Metal Complex Catalysts 109
3.3 Summary and Outlook 113
References 113

4 Olefin Polymerization with Non-metallocene Catalysts (Late Transition Metals). 119
Daisuke Takeuchi
4.1 Introduction: Brief History of Late Transition Metal Catalysts for Olefin Polymerization 120
4.2 Polymerization of Olefins Catalyzed by Cationic Pd and Ni Complexes with Neutral Ligands 121
4.2.1 Cationic Ni and Pd Catalysts with Diimine Ligands 122
4.2.2 Cationic Complexes with Other Bidentate Neutral Ligands 132
4.2.3 Cationic Complexes with Monodentate and Tridentate Ligands 133
4.3 Polymerization of Olefins by Neutral Pd and Ni Complexes with Monoanionic Ligands 134

4.3.1 Neutral Complexes with Monoanionic N-O Ligands 134
4.3.2 Phosphinesulfonate Complexes of Pd 138
4.3.3 Neutral Complexes with Other Monoanionic Ligands . . . 140
4.4 Polymerization of Olefins by Fe and Co Complexes 141
4.5 Polymerization of Olefins by Other Late Transition Metal Catalysts 146
4.6 Multimetallic Catalysts. 146
4.7 Olefin Polymerization in Aqueous Media 149
4.8 Cyclopolymerization of Non-conjugated Dienes 150
4.9 Summary 153
References 154

5 Oligomerization of Olefins 169
Daisuke Takeuchi and Kohtaro Osakada
5.1 Introduction 169
5.2 Oligomerization of Ethylene 170
5.2.1 General Aspect 170
5.2.2 Ethylene Oligomerization to Olefins with Schulz–Flory Distribution and Dimerization. 171
5.2.3 Ethylene Oligomerization to α-Olefins with Poisson Distribution 176
5.3 Selective Trimerization of Ethylene 177
5.3.1 Chromium Catalyst 177
5.3.2 Titanium Catalyst 189
5.3.3 Tantalum Catalyst 192
5.3.4 Ruthenium Catalyst 193
5.4 Tetramerization of Ethylene 194
5.4.1 Effect of Ligand Structure 195
5.4.2 Effect of Cocatalysts and Additives. 199
5.4.3 Mechanism of Cr-Catalyzed Ethylene Tetramerization. . . 200
5.5 Dimerization of α-Olefins 201
5.6 Trimerization of α-Olefins 204
5.7 Cooligomerization of Ethylene and α-Olefins 205
5.8 Cooligomerization of Other Vinyl Monomers 206
5.9 Summary 207
References 207

6 Polymerization of Polar Monomers. 217
Kyoko Nozaki
6.1 Introduction 217
6.2 Coordination-Addition Polymerization of Polar Monomers 218
6.3 Block Copolymerization of Polar Monomers and Non-polar Monomers 221

6.4 Random Copolymerization of Polar Monomers and Non-polar Monomers 221
6.4.1 General Aspects on Coordination-Insertion Polymerization of Polar Vinyl Monomers 223
6.4.2 Diimine/Pd or Ni Catalyst 224
6.4.3 Phosphine-Sulfonate/Pd Catalyst 229
6.5 Copolymerization of Polar Monomers with Other Monomers . . . 232
6.6 Conclusions and Outlook 234
References 234

7 Metathesis and Polymerization 237
Kohtaro Osakada
7.1 Introduction 237
7.2 Catalysts 240
7.2.1 Multicomponent Catalysts 240
7.2.2 Homogeneous Catalysts 241
7.3 Application of Olefin Metathesis 249
7.3.1 Synthesis of the Polymers with New Structures and Functionality 249
7.3.2 Synthesis and Reactions of the Ligand of Transition Metal Complexes 252
7.3.3 Synthesis of Natural Products 257
7.3.4 Interlocked Molecules 260
7.4 Conclusion 266
References 266

8 Cross-Coupling Polymerization 271
Take-aki Koizumi and Takaki Kanbara
8.1 Introduction 271
8.2 Ni-Catalyzed Polycondensation 272
8.3 Pd-Catalyzed Polycondensation 276
8.4 Cu-Catalyzed Polycondensation 289
8.5 Recent Topics of the Polymers Synthesized by Using Cross-Coupling Polymerization Methods 291
8.6 Summary 297
References 297

Chapter 1
Olefin Polymerization with Metallocene Catalysts

Takeshi Shiono

Abstract This chapter firstly explains the basic terms and concepts concerning olefin polymerization and polymer synthesis, and then provides comprehensive yet concise commentaries on olefin polymerization by metallocene catalysts. In Sect. 1.1 (Introduction), the history of olefin polymerization catalysts is briefly reviewed with a focus on the uniformity of the active species. In Sect. 1.2 are described the elementary process of olefin polymerization by transition metal catalysts and the molecular weight distributions of produced polymers. The tacticity and stereoregularity of vinyl polymer are explained in Sect. 1.3, where the relation between the microtacticity of the stereoregular polymer and the mechanism of stereospecific polymerization is described in detail. Section 1.4 deals with copolymerization with two kinds of monomers on the basis of kinetics and probability theory. In Sect. 1.5, are described the basics of metallocene catalysts and their characteristics in propylene polymerization and copolymerization of olefins.

1.1 Introduction

Polyolefins are currently the most important synthetic polymers with the largest commercial production. Polyethylene and polypropylene are representative polyolefins. Polyethylene is classified into three categories, i.e., low-density polyethylene produced by high-pressure radical polymerization, high-density polyethylene and linear low-density polyethylene, which are homo- and copolymers of ethylene with 1-alkene, obtained by Phillips and Ziegler–Natta catalysts. Polypropylene possessing stereoregular structure is produced only by Ziegler–Natta catalysts. Since the great finding of Ziegler [1] and Natta [2], many

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researchers have paid enormous effort to improve the catalytic performance of heterogeneous Ti-based Ziegler–Natta catalysts such as activity, the control of molecular weight and molecular weight distribution, copolymerization ability, stereospecificity, the control of polymer particle size and shape, etc. Consequently, highly active $MgCl_2$-supported $TiCl_4$ catalysts are widely used for the commercial production of polyethylene and polypropylene [3, 4].

Homogeneous Ziegler–Natta catalysts composed of titanocene compound and alkylaluminum were also found in the middle of 1950s [5, 6]. Their application had been limited to the basic study because they showed low activity in ethylene polymerization and no activity in propylene polymerization. However, it was reported that the addition of a small amount of water improved the catalytic activity of those systems [7]. Sinn and Kaminsky isolated the condensation product of trimethylaluminum and water, i.e., methylaluminoxane (MAO), and applied it as a cocatalyst for zirconocene and titanocene compounds to obtain highly active homogeneous Ziegler–Natta catalysts for ethylene and propylene polymerizations [8]. The catalytic system was found to be active also for homo- and copolymerization of higher 1-alkene or cycloolefin with ethylene as well as for stereospecific polymerization of propylene by tuning the metallocene used [9]. The activation methods except MAO were developed and the homogeneous systems were successfully heterogenized in order to apply them to slurry phase or gas phase process [10, 11]. These catalytic systems which composed of a metallocene compound are called metallocene catalysts.

Most important characteristics of metallocene catalysts is the uniformity of the active species regardless of the phase of the catalytic systems, which gives uniform polymers with respect to molecular weight distribution, comonomer composition, stereoregularity, etc. Those uniform polyolefins cannot be obtained with $TiCl_3$- or $TiCl_4$-based heterogeneous Ziegler–Natta catalysts because of their non-uniformity of the active species. The words "homogeneous" and "heterogeneous" are usually used to describe the phase of catalytic systems, but a homogeneous catalyst does not necessarily gives homogeneous (uniform) active species. In order to clarify the homogeneity or the inhomogeneity of active species in a polymerization catalyst, we currently use the word "single-site" or "multi-site".

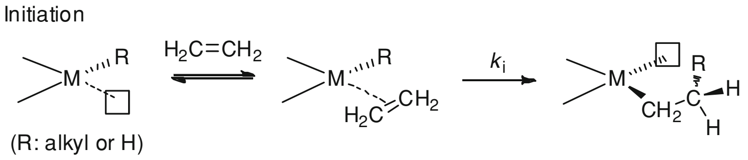
The founding of metallocene catalysts stimulated the research on the polymerization catalysts composed of well-characterized transition metal complexes, which has evolved in a variety of single-site catalysts such as half metallocene catalysts (composed of a monocyclopentadienyl compound), constrained geometry catalyst (composed of an *ansa*-(cyclopentadienyl)(amido) compound), Brookhart catalyst (composed of a late transition metal diimine compound), FI catalyst (composed of a bis(phenoxyimine) compound) [12].

This chapter first explains the basic terms and the concepts in the fields of polymer chemistry and olefin polymerization catalysis, and then describes the characteristics of metallocene catalysts.

1.2 Elementary Processes of Olefin Polymerization

1.2.1 Initiation and Propagation Reactions

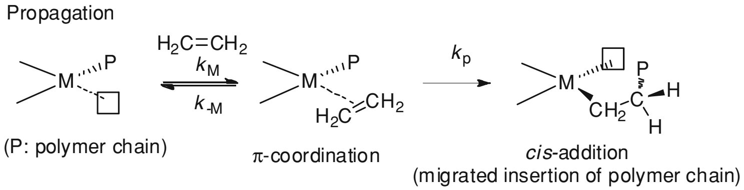
Olefin polymerization with Ziegler–Natta catalyst is initiated by the coordination of olefin to a coordinatively unsaturated transition metal–alkyl or metal–hydride species followed by the insertion of the coordinated olefin (Eq. 1.1).



(1.1)

Olefin coordination to a transition metal is dominated by the σ-bond via the electron donation of the C=C π bond to the empty *d* orbital on the metal and the back donation from the filled metal *d* orbital to the empty π* orbital as shown Fig. 1.1.

The insertion reaction proceeds via alkyl migration to the coordinated olefin (*cis*-addition), and successive multiple coordination-insertions of olefins propagate a polymer chain. This type of polymerization is therefore classified to coordination polymerization. If steady-state approximation is applied to the olefin-coordinated metal–alkyl species, propagation rate R_p is expressed by Eq. 1.3, where [C*] and [M] are the concentrations of active species and monomer, respectively. When the coordination of monomer is very strong or very weak, Eq. 1.3 can be approximated by $R_p = k_p\,[C^*]$ or $R_p = \{k_p k_M/(k_{-M} + k_p)\}\,[C^*]\,[M]$, respectively.



(1.2)

$$R_p = \frac{k_p\, k_M\, [C^*]\, [M]}{k_M\, [M] + k_{-M} + k_p} \qquad (1.3)$$

R_p: polymerization rate

[C*]: number of active species

[M]: monomer concentration

1.2.2 Chain Transfer and Termination Reaction

Main chain transfer reactions in olefin polymerization with Ziegler–Natta catalyst is β-hydrogen transfer to the coordinated olefin (Eq. 1.4) or to the metal center

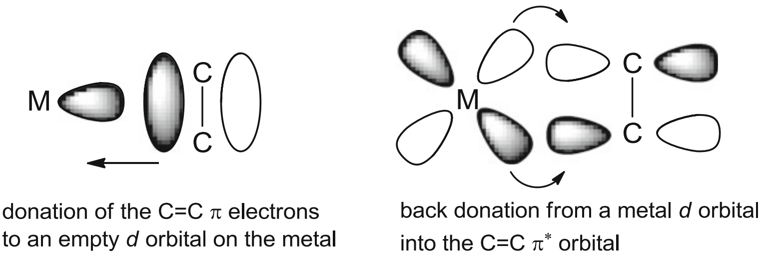
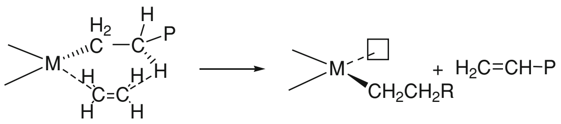


Fig. 1.1 Coordination mode of olefin to a transition metal

(Eq. 1.5), and the alkyl exchange between the active species and an alkylmetal used as a cocatalyst (Eq. 1.6).

Chain transfer



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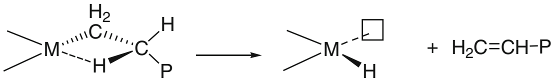
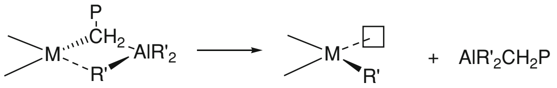
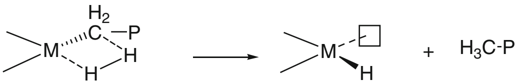


(1.5)



(1.6)

In a commercial process, hydrogen gas is used as a chain transfer reagent (Eq. 1.7).



(1.7)

In all cases, transition metal–alkyl or metal–hydride is regenerated and the propagation reaction continues.

Termination reaction, i.e., the deactivation of catalyst is considered to proceed via homolytic cleavage of the transition metal–polymer bond by unimolecular or bimolecular process to cause the reduction of the active transition metal.

1.2.3 Molecular Weight and Molecular Weight Distribution

1.2.3.1 Average Molecular Weight

Every synthetic polymer contains molecules of various degrees of polymerization or molecular weight. This state of affairs is described that the polymer shows polydispersity with respect to degree of polymerization or molecular weight. Accordingly, we can obtain the degree of polymerization or the molecular weight of polymer only as an average value. The number-average polymerization degree $\bar{P}_\mathrm{n}$ and the weight-average polymerization degree $\bar{P}_\mathrm{w}$ are defined by Eqs. 1.8 and 1.9 where x is a polymerization degree of a certain polymer chain "x-mer" and N_x is the number of x-mer. The number-average and the weight-average molecular weights, $\overline{M}_\mathrm{n}$ and $\overline{M}_\mathrm{w}$, are obtained by multiplying the molecular weight of the monomer, M_0, to $\bar{P}_\mathrm{n}$ and $\bar{P}_\mathrm{w}$, respectively (Eqs. 1.10 and 1.11).

$$\bar{P}_\mathrm{n} = \frac{\sum x \cdot N_x}{\sum N_x} \tag{1.8}$$

$$\bar{P}_\mathrm{w} = \frac{\sum x^2 \cdot N_x}{\sum x \cdot N_x} \tag{1.9}$$

$$\overline{M}_\mathrm{n} = \overline{P}_\mathrm{n} M_0 \tag{1.10}$$

$$\overline{M}_\mathrm{w} = \overline{P}_\mathrm{w} M_0 \tag{1.11}$$

1.2.3.2 Molecular Weight Distribution

In vinyl-addition polymerization, the molecular weight of the produced polymer is determined by the relative ratio of propagation and termination reactions. Suppose that coordination polymerization proceeds in a steady state, and put the propagation rate and the total rate of chain transfer and termination as r_p and Σr_tr, respectively. Then, the propagation probability α is given by

$$\alpha = \frac{r_p}{r_p + \sum r_{tr}} \tag{1.12}$$

The mole fraction of "x-mer", $f_\mathrm{n}(x)$, is shown by Eq. 1.13, because "x-mer" forms via $(x - 1)$ times of propagation followed by termination.

$$f_n(x) = \alpha^{x-1} \cdot (1 - \alpha) \tag{1.13}$$

The weight fraction of "x-mer", $f_\mathrm{w}(x)$, is

$$f_w(x) = x \cdot \alpha^{x-1} \cdot (1-\alpha)^2 \tag{1.14}$$

Please note $f_\mathrm{n}(x)$ and $f_\mathrm{w}(x)$ are normalized. Referring Eqs. 1.8 and 1.9, $\overline{P}_\mathrm{n}$ and $\overline{P}_\mathrm{w}$ are expressed by $f_\mathrm{n}(x)$ and x, and converted to the equations with α by summation of series with x.

$$\overline{P}_\mathrm{n} = \sum_{x=1}^{\infty} x \cdot f_n(x) = \frac{1}{1-\alpha} \tag{1.15}$$

$$\overline{P}_\mathrm{w} = \sum_{x=1}^{\infty} x \cdot f_w(x) = \frac{1+\alpha}{1-\alpha} \tag{1.16}$$

Thus, we obtain $\overline{P}_\mathrm{w}/\overline{P}_\mathrm{n}$ ($\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$) as

$$\overline{P}_\mathrm{w}/\overline{P}_\mathrm{n} = \overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} = 1 + \alpha \tag{1.17}$$

This ratio is named the polydispersity index (PDI) or the polydispersity. When high molecular-weight polymer is obtained, α should be close to one. Thus $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} = 2$. Figure 1.2 illustrates the distribution of x-mer in the polymers with $\overline{P}_\mathrm{n} = 10$ ($\alpha = 0.9$) and $\overline{P}_\mathrm{n} = 100$ ($\alpha = 0.99$).

If the system is not uniform chemically or physically with respect to the propagation probability α, PDI becomes more than 2.

It should be noted that Eqs. 1.13–1.17 are the same with those of condensation polymerization by substituting α with p; p is an extent of polymerization. α is independent of polymerization time in a steady state, whereas p reaches to unity with the progress of polymerization. Although α and p have a different definition, both parameters imply the bonding probability of the neighboring monomers. The molecular weight distribution expressed by Eqs. 1.13 or 1.14 are called the most probable (or Schulz–Flory) distribution.

1.2.3.3 Living Polymerization

In an ideal living polymerization, all the active species simultaneously initiate the polymerization, with the rate constant for initiation greater than that for propagation and with neither chain transfer nor termination. Under these conditions, we can obtain a polymer with very narrow molecular weight distribution. The kinetic treatment on this model, where polymerization time is replaced with a number of average polymerized monomer per one active species v, gives $f_\mathrm{n}(x)$ and $f_\mathrm{w}(x)$ as Poisson distribution.

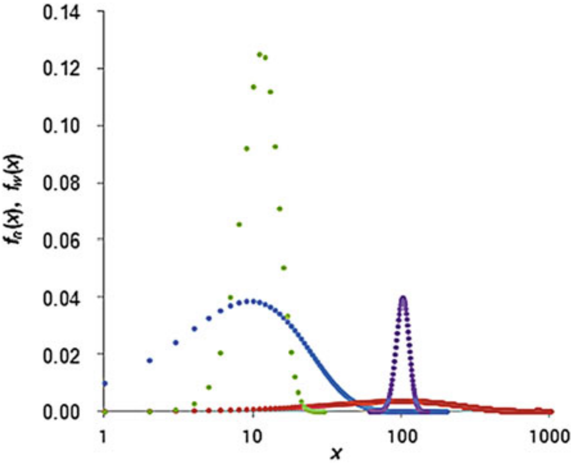


Fig. 1.2 Distribution of x-mer in the polymers with $\overline{P}_\mathrm{n} = 10$ and $\overline{P}_\mathrm{n} = 100$: ●, ●, the most probable distribution; ●, ●, Poisson distribution

$$f_n(x) = \frac{v^{x-1}}{(x-1)!} \cdot e^{-v} \tag{1.18}$$

$$f_w(x) = \frac{v}{v+1} \cdot x \cdot \frac{v^{x-2}}{(x-1)!} \cdot e^{-v} \tag{1.19}$$

$\overline{P}_\mathrm{n}$ and $\overline{P}_\mathrm{w}$ expressed by x and $f_\mathrm{n}(x)$ are converted to the function of v by summation of series with x,

$$\overline{P}_\mathrm{n} = v + 1 \tag{1.20}$$

$$\overline{P}_\mathrm{w} = \frac{v^2 + 3v + 1}{v + 1} \tag{1.21}$$

The polydispersity index is

$$\begin{aligned} \frac{\overline{P}_\mathrm{w}}{\overline{P}_\mathrm{n}} &= \frac{v^2 + 3v + 1}{(v+1)^2} = 1 + \frac{v}{(v+1)^2} \\ &\approx 1 + \frac{1}{v+1} = 1 + \frac{1}{\overline{P}_\mathrm{n}} \end{aligned} \tag{1.22}$$

where the approximation applies for large v. Equation 1.22 indicates that the polydispersity gets close to one according to the progress of polymerization. The distributions of x-mer in the polymers with $\overline{P}_\mathrm{n} = 10$ $(v = 9)$ and $\overline{P}_\mathrm{n} = 100$ $(v = 99)$ are illustrated in Fig. 1.2.

1.3 Structure of Vinyl Polymer and Stereospecific Polymerization

1.3.1 Stereoregularity of Vinyl Polymer

In the polymerization of substituted olefins such as propylene and methyl methacrylate, chiral carbons are induced in the main chain. If the molecular weight of the produced polymer is high enough to neglect the chain end structure of the initiation and the termination, we can only distinguish the relative configuration of the adjacent monomer units. In the adjacent two monomer units (diad), the substituted carbons have the same configuration or the opposite one. The former is meso denoted by m, and the latter is racemo denoted by r, respectively (Fig. 1.3). Then, the stereo structure, i.e., the tacticity of the adjacent three monomer units are expressed by mm (isotactic triad), rr (syndiotactic triad), and mr (or rm, heterotactic triad); mr and rm are identical in vinyl polymers.

An arbitrary stereo sequence can be expressed by the sequence of m and r. The polymer composed of m sequences, •••mmmmmm•••, that composed of r sequences, •••rrrrrr•••, and that composed of random sequences of m and r are named isotactic, syndiotactic and atactic, respectively [13]. The physical properties of vinyl polymers strongly depend on the stereoregularity of the polymers. The control of tacticity is therefore very important in vinyl polymerization.

The tacticity of vinyl polymer can be evaluated by NMR in principal. In the $^{13}C\{^1H\}$ NMR spectrum of polypropylene, the resonance of methylene carbon is split by diad tacticities and those of methyl and methine carbons are split by triad tacticities. These resonances are further split by the stereoregularity of the neighboring propylene units at both sides, i.e., tetrad and pentad tacticities, respectively. The resonance of methyl carbon is the most sensitive to the stereoregularity of polypropylene, and the pentad tacticities can be determined by 125 MHz $^{13}C\{^1H\}$ NMR (Fig. 1.4).

1.3.2 Regiochemistry in Propylene Polymerization

Coordination polymerization of olefin proceeds via insertion of coordinating monomer to metal–polymer bond. In the case of 1-alkene such as propylene, two insertion modes which differ in regiochemistry are possible; C1 carbon of olefin is attached to the metal (primary insertion or 1,2-insertion) or vice versa (secondary insertion or 2,1-insertion) (Fig. 1.5).

For the connection of the neighboring monomer units, there are three possibilities; C1 carbon connects to C2 carbon (head-to-tail), C1 carbon connects to C1 carbon (tail-to-tail), or C2 carbon connects to C2 carbon (head-to-head). The polymerization should proceed regioselectively in order to produce stereoregular polymers. The propylene polymerization with Ti-based heterogeneous

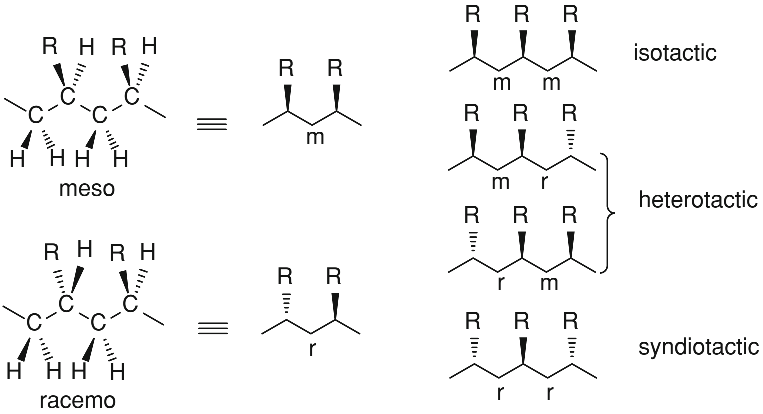


Fig. 1.3 Stereoregularity of vinyl polymer

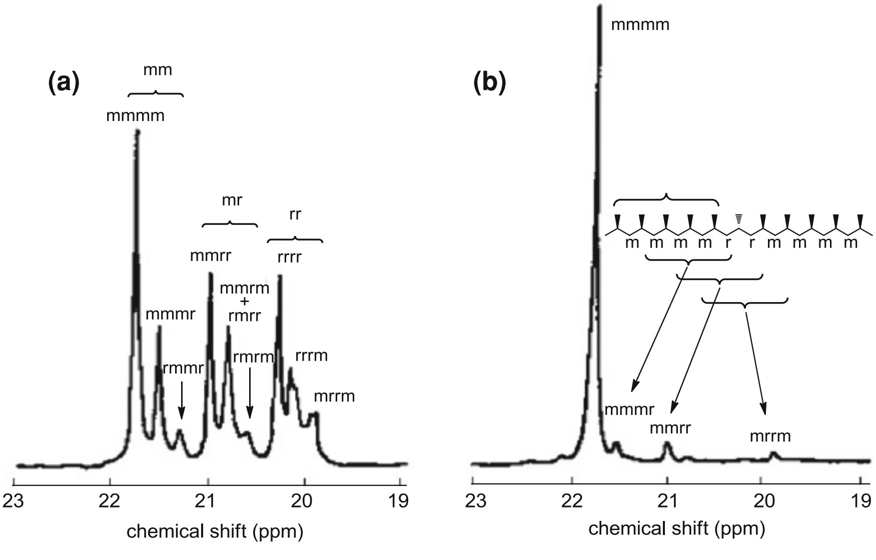


Fig. 1.4 125 MHz $^{13}C\{^1H\}$ NMR spectra of typical polypropylene obtained $TiCl_4/MgCl_2$–Et_3Al; **a** boiling heptane-soluble fraction, **b** boiling heptane-insoluble fraction

Ziegler–Natta catalysts and zirconocene catalysts proceeds via 1,2-insertion in high regioselectivity. Some zirconocene catalysts occasionally cause 2,1-insertion to give an isolated inverted unit or a tetramethylene unit via β-hydrogen elimination of methyl group and re-insertion (Fig. 1.6) [14, 15].

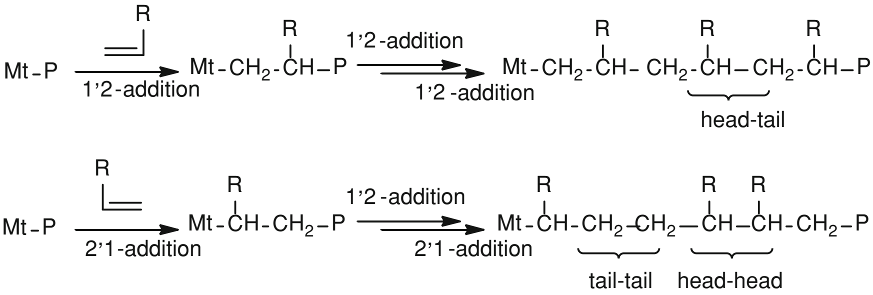


Fig. 1.5 Regiochemistry of propylene insertion to metal–polymer bond

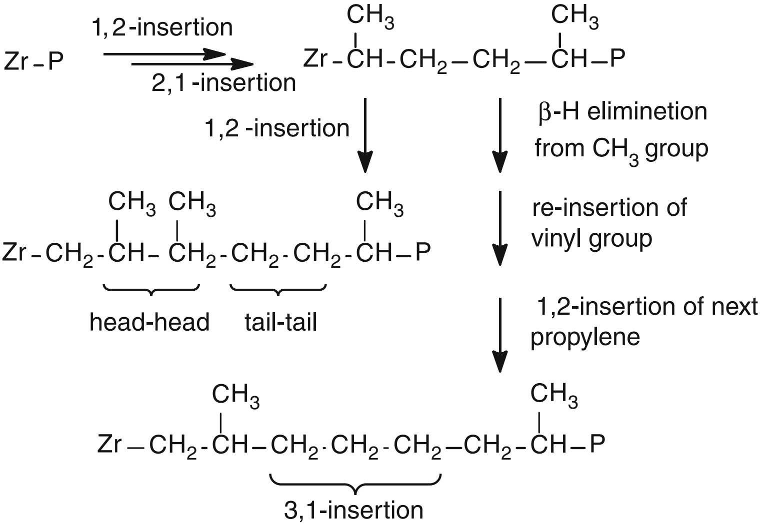


Fig. 1.6 3,1-insertion of propylene to Zr-polymer bond

1.3.3 Origin of Stereospecificity

Propylene is a prochiral molecule where sp^2-hybridized C2 carbon is converted to a chiral carbon when a metal–polymer bond is added to the *re* or *si* face of the molecule. Since the propagation proceeds via the coordination of propylene followed by the *cis*-addition of metal–polymer bond, the configuration of the chiral carbon induced in the main chain is determined when propylene coordinates to the metal center. Thus, the active species should differentiate the prochiral faces of propylene to achieve stereospecific polymerization.

In principal, the active species of propylene polymerization possess two chiral structures; one is the chiral carbon of the last-inserted propylene unit and the other

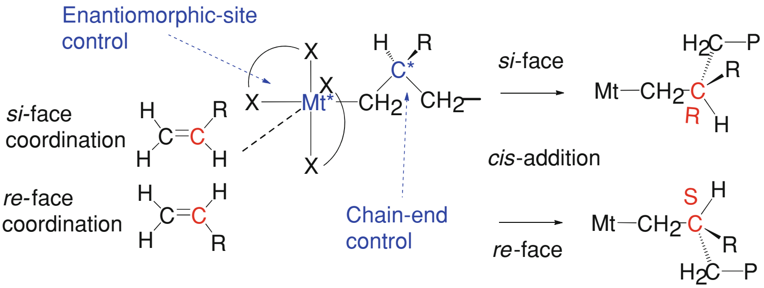


Fig. 1.7 Mechanism of stereospecific polymerization of 1-alkene

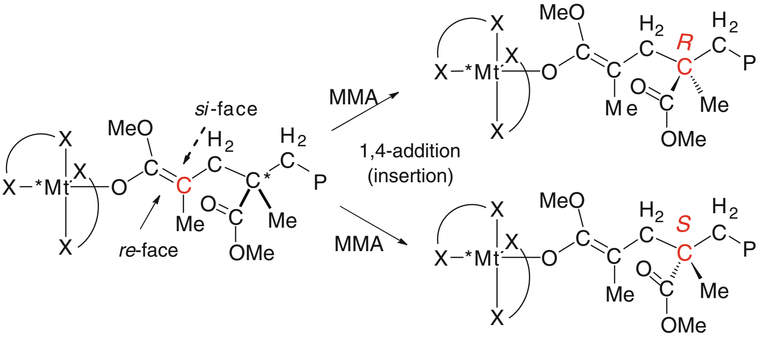


Fig. 1.8 Mechanism of stereospecific polymerization of methyl methacrylate

is the chirality of the metal center caused by the ligand structure [16]. The selection of the prochiral faces with these chiral centers are named chain-end control and enantiomorphic-site control (or catalytic-site control), respectively (Fig. 1.7). If these chiral center continuously select the same prochiral face (*re–re–re*••• or *si–si–si*•••), isotactic polymer is produced. Whereas syndiotactic polymer is produced by alternating selection of *re* and *si* faces.

It should be noted that certain metallocene catalysts also conduct the stereospecific polymerization of methyl methacrylate and its derivatives. In this case, the active species is a metal enolate, and the configuration of the chiral carbon induced in the main chain is determined by the selection of the prochiral faces of the enolate (Fig. 1.8).

1.3.4 Polymerization Mechanism and Microtacticity

1.3.4.1 Chain-End Control

In a chain-end controlled mechanism, the chiral carbon at the propagation chain-end selects the prochiral face of incoming monomer. Thus, if the probability that

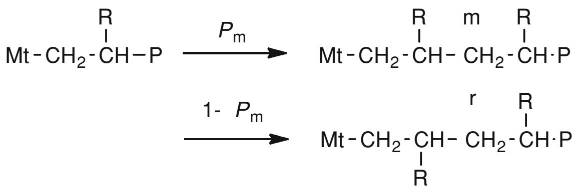


Fig. 1.9 Stereospecific polymerization by a chain-end control: the case of 1,2-insertion is shown

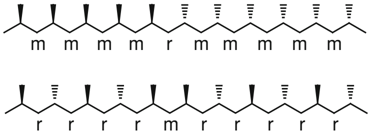


Fig. 1.10 Characteristic stereodefects formed by a chain-end controlled mechanism

the chain-end carbon selects the prochiral face to induce the same chirality is set to P_{m}, P_{m} is the probability of m diad formation. The probability of r diad formation P_{r} equals to $(1 - P_{\mathrm{m}})$: $P_{\mathrm{m}} > 0.5$ and $P_{\mathrm{m}} < 0.5$ indicate isotactic-specific and syndiotactic-specific polymerization (Fig. 1.9). In the case of $P_{\mathrm{m}} = 0.5$, statistically atactic polymer is produced.

P_{m} (P_{r}) is independent of the proceeding diad, and the distribution of m and r in the polymer obeys a Bernullian statics. Thus, the probability of any stereo sequence is expressed by one probability P_{m} or P_{r}. For example, diad and triad are expressed by P_{m} as follows [17].

$$[\mathrm{m}] = P_{\mathrm{m}}; \quad [\mathrm{r}] = 1 - P_{\mathrm{m}} \tag{1.23}$$

$$[\mathrm{mm}] = P_{\mathrm{m}^2}; \quad [\mathrm{mr}] = [\mathrm{rm}] = 2P_{\mathrm{m}}(1 - P_{\mathrm{m}}); \quad [\mathrm{rr}] = (1 - P_{\mathrm{m}})^2 \tag{1.24}$$

Thus, the steric triads of the polymer produced by a chain-end controlled mechanism satisfy the following equation.

$$4[\mathrm{mm}]\,[\mathrm{rr}]/[\mathrm{mr}]^2 = 1 \tag{1.25}$$

In the isotactic-specific polymerization by a chain-end controlled mechanism, when the prochiral face is miss-selected, the chirality of the chain-end carbon is inverted and the opposite prochiral face is successively selected. Hence, the isolated r diad in m sequence is the characteristic stereodefect. Whereas, the isolated m diad in r sequence is the characteristic stereodefect in the syndiotactic-specific polymerization by a chain-end controlled mechanism (Fig. 1.10).

The selectivity of the prochiral faces is not high in a chain-end controlled mechanism, because the coordination of the monomer to the metal (Mt) is regulated by the chiral carbon which located one σ-bond away in the case of 2,1-insertion, Mt–C*H(R)–P, or two σ-bond away in the case of 1,2-insertion, Mt–C–C*H(R)–P. Thus a low temperature is necessary for stereospecific polymerization by a chain-end controlled mechanism.

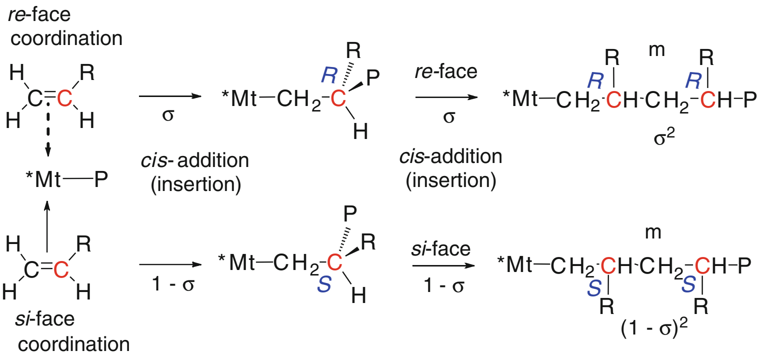


Fig. 1.11 Formation of m diad by an enantiomorphic-site controlled mechanism on *re*-face preferential site

1.3.4.2 Enantiomorphic-Site Control

In an enantiomorphic-step controlled mechanism, a chiral metal center selects the prochiral face of coordinating monomer. Thus, if the probability that the metal center selects one of the prochiral faces is set to σ, steric diad and triad are expressed as follows [18] (Fig. 1.11).

$$[\mathrm{m}] = [RR] + [SS] = \sigma^2 + (1 - \sigma)^2 \tag{1.26}$$

$$[\mathrm{r}] = [RS] + [SR] = 2\sigma(1 - \sigma) \tag{1.27}$$

$$[\mathrm{mm}] = [RRR] + [SSS] = \sigma^3(1 - \sigma)^3 \tag{1.28}$$

$$\begin{aligned}[\mathrm{mr}] = [\mathrm{rm}] &= [RRS] + [SSR] + [RSS] + [SRR] \\ &= 2\sigma^2(1 - \sigma) + 2\sigma(1 - \sigma)^2\end{aligned} \tag{1.29}$$

$$[\mathrm{rr}] = [RSR] + [SRS] = \sigma^2(1 - \sigma) + \sigma(1 - \sigma)^2 \tag{1.30}$$

Thus,

$$[\mathrm{mr}] : [\mathrm{rr}] = 2 : 1 \tag{1.31}$$

Even if the metal center accidentally selects the other prochiral face with the probability of 1 − σ, the original prochiral face of the successive monomer is selected with the probability of σ by the stereorigid chiral metal center. Therefore rr diad in m sequences is the characteristic stereodefect in the isotactic polymer formed by an enantiomorphic-site controlled mechanism: the steric pentad satisfy the following relation; [mmmr]:[mmrr]:[mrrm] = 2:2:1.

Syndiotactic polymer by an entiomorphic-site controlled mechanism is produced when the chiral active center isomerizes to the antipode after each monomer

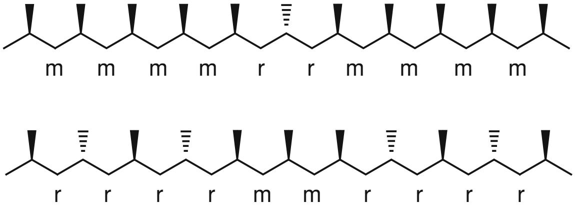


Fig. 1.12 Characteristic stereodefects formed by an enantiomorphic-site controlled mechanism

insertion. Consequently, *re*- and *si*-face are alternating selected to form syndiotactic polymer. If the *re*-face selectivity of the chiral metal center is set to λ, the *si*-face selectivity of the antipode is also λ. Thus, the following relations are derived in diad and triad.

$$[\mathrm{r}] = \lambda^2 + (1-\lambda)^2, \quad [\mathrm{m}] = 2\lambda(1-\lambda) \tag{1.32}$$

$$[\mathrm{rr}] = \lambda^3 + (1-\lambda)^3 \tag{1.33}$$

$$[\mathrm{mr}] = [\mathrm{rm}] = 2\lambda^2(1-\lambda) + 2\lambda(1-\lambda)^2 \tag{1.34}$$

$$[\mathrm{mm}] = \lambda^2(1-\lambda) + \lambda(1-\lambda)^2 \tag{1.35}$$

Thus,

$$[\mathrm{rm}] : [\mathrm{mm}] = 2 : 1 \tag{1.36}$$

If the chiral center which prefers *re*-face occasionally selects *si*-face or vice versa with the probability of $1-\lambda$, the same prochiral face is consecutively selected in three times to form isolated mm triad in syndiotactic sequence (Fig. 1.12). When the chiral center isomerizes to the antipode without monomer insertion, the same prochiral face is consecutively selected in two times to form isolated m diad in syndiotactic sequence. This stereodefect is the same with that formed in a syndiotactic polymer by a chain end-controlled mechanism.

1.3.4.3 Polypropylene Obtained by Ziegler–Natta Catalysts

Isotactic polypropylene is currently produced by Ti-based heterogeneous Ziegler Natta catalysts. The polypropylenes obtained can be fractionated by boiling heptane. The weight fraction of heptane-insoluble part, called as isotactic index (I.I.), is used for evaluating the isotactic-specificity of catalyst. We should keep in mind that I.I. is the ratio of non-stereospecific and stereospecific sites and does not indicate the selectivity of prochiral face at an isotactic-specific site. Kakugo et al. fractionated isotactic polypropylenes obtained with β-$TiCl_3$–$AlEt_2Cl$ (mmmm = 94.5 %, $\bar{M}_n$ = 252,000) and δ-$TiCl_3$–$AlEt_2Cl$ (mmmm = 97.5 %, $\bar{M}_n$ = 315,000) by an elution column technique, where the temperature of elute was gradually increased [19]. They analyzed each fraction by GPC, DSC and $^{13}C\{^1H\}$ NMR in

Fig. 1.13 Cumulative and differential fractionation curves, and the melting temperatures and the isotactic pentads (mmmm) of the fractions. Catalyst systems: (○)β-$TiCl_3$-Et_2AlCl; (□)δ-$TiCl_3$-Et_2AlCl [19]

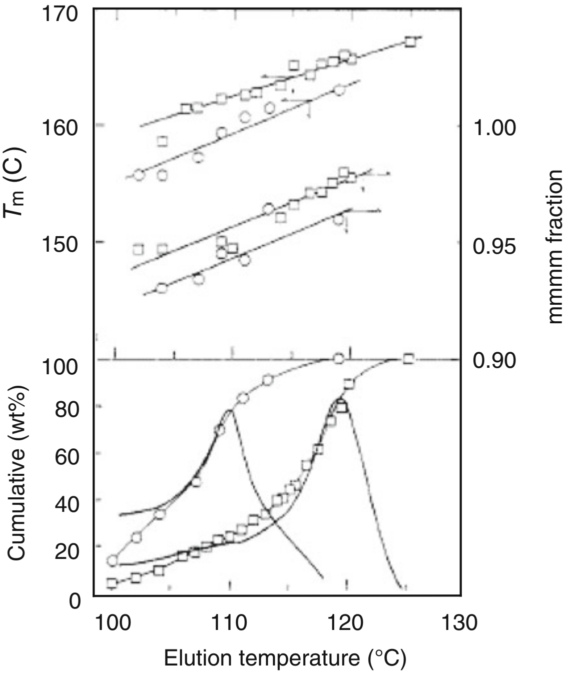
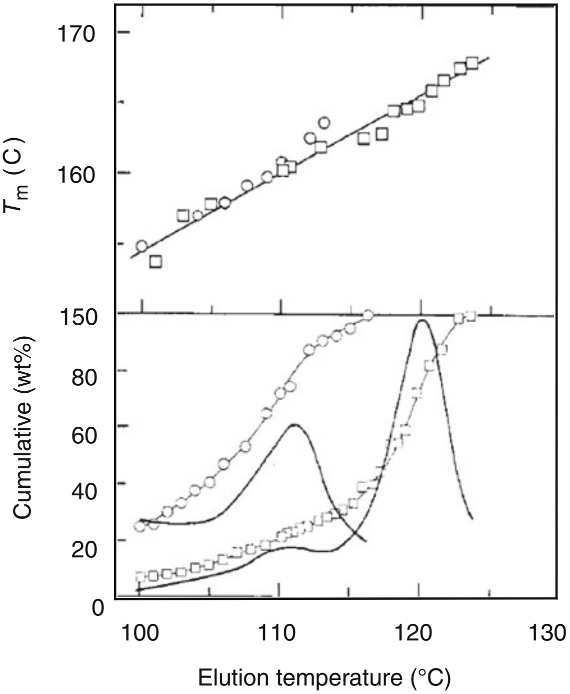


Fig. 1.14 Cumulative and differential fractionation curves, and the melting temperatures of each fraction. Catalyst systems: $MgCl_2$-supported Ti–Et_3Al with (□) and without (○) methyl *p*-toluate [19]



detail and displayed the microtacticity distribution of the isotactic polypropylenes as shown in Fig. 1.13, which clearly indicates that the active site of δ-$TiCl_3$ is more isotactic-selective than that of β-$TiCl_3$.

They applied this technique to investigate the additive effects of Lewis base on propylene polymerization with a $MgCl_2$-supported Ti-based catalyst and clarified that the addition of methyl *p*-toluate suppressed the formation of isotactic-selective site with low σ value and newly gave the isotactic-selective site with high *σ* value. (Fig. 1.14).

This technique is named Temperature Rising Elution Fractionation (TREF) and applied also for ethylene-based copolymers.

The microtacticity of heptane-soluble atactic polypropylene (Fig. 1.4a) was well-characterized by the combination of syndiotactic sequence with a chain-end controlled mechanism and isotactic sequence with an enantiomorphic-site controlled mechanism, suggesting that the polypropylenes should have a stereoblock structure [20].

1.4 Copolymer and Copolymerization

1.4.1 *Structure of Copolymers*

If we consider a linear copolymer consisted of two different monomers, M_1 and M_2, three typical structures can be considered; random, alternate and block structures as shown in Fig. 1.15. Random copolymer is the copolymer in which the comonomer sequence distribution obeys a Bernoullian statics. Copolymer in which the comonomer sequence distribution obeys a known statistical law is named statistical copolymer, and expressed by poly(M_1-*stat*-M_2). Although random copolymer is a special case of statistical copolymers, the word “random” is not clearly distinguished from “statistical” and frequently used for the copolymer where comonomer composition is controlled freely.

1.4.2 *Copolymerization*

We can synthesize homopolymers with various physical properties by controlling molecular weight, molecular weight distribution and stereoregularity. If we can introduce second monomer freely at the place we want as shown in Fig. 1.15, the kinds of polymers obtained are almost unlimited. Thus, copolymerization is very important to synthesize a wide variety of polymers from a few limited monomers. Polyolefin is a good example. Crystallinity of polyethylene is controlled by introducing 1-alkene (linear low density polyethylene, LLDPE), and elastomer is obtained by copolymerization of ethylene and propylene (EPR). Crystallinity of isotactic polypropylenes is also controlled by introducing a small amount of ethylene or 1-butene, and the product is called random polypropylene.

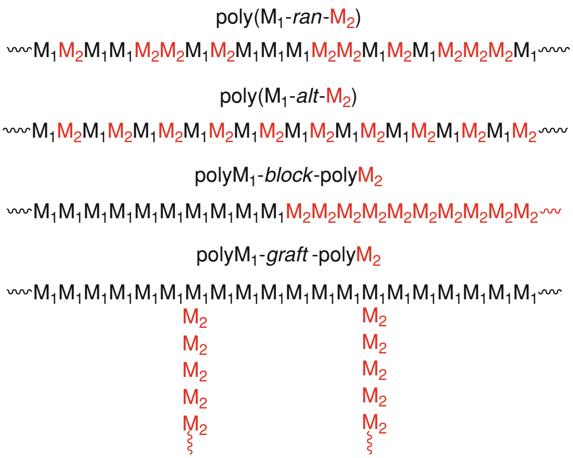


Fig. 1.15 Structures of copolymers, poly(M1-*co*-M2) or copoly(M1/M2)

1.4.2.1 Kinetic Treatment

We consider binary copolymerization of two monomers, M_1 (ethylene) and M_2 (propylene or 1-alkene) as the simplest case [21, 22]. The copolymerization consists of initiation, propagation, chain transfer and/or termination reaction. When the copolymerization proceeds in a steady state to produce high molecular weight copolymer, we can concentrate on the propagation reaction to consider the comonomer composition in the copolymer. If the insertion of M_2 is regioselective and the reactivity of the active species is determined by the last inserted monomer unit, the propagation reaction involves the following four reactions, where the catalytic center is shown with Ti for descriptive purposes. It should be noted that the system should be treated as the ternary copolymerization consisted of M_1, 1,2-inserted M_2 and 2,1-inserted M_2 units when the insertion of M_2 is not regioselective.

$$\sim M_1{-}\mathrm{Ti} \quad + \quad M_1 \xrightarrow{k_{11}} \sim M_1M_1{-}\mathrm{Ti} \tag{1.37}$$

$$\sim M_1{-}\mathrm{Ti} \quad + \quad M_2 \xrightarrow{k_{12}} \sim M_1M_2{-}\mathrm{Ti} \tag{1.38}$$

$$\sim M_2{-}\mathrm{Ti} \quad + \quad M_1 \xrightarrow{k_{21}} \sim M_2M_1{-}\mathrm{Ti} \tag{1.39}$$

$$\sim M_2{-}\mathrm{Ti} \quad + \quad M_2 \xrightarrow{k_{22}} \sim M_2M_2{-}\mathrm{Ti} \tag{1.40}$$

Here k_{ij} is the rate constant of step ij, and the subscripts 1 and 2 refer to M_1 and M_2, respectively.

Thus the consumption rates of M_1 and M_2 are

$$\frac{d[M_1]}{dt} = k_{11}[C_1^*][M_1] + k_{12}[C_1^*][M_2] \tag{1.41}$$

$$\frac{d[M_2]}{dt} = k_{21}[C_2^*][M_1] + k_{22}[C_2^*][M_2] \tag{1.42}$$

Here $[C_1^*]$ and $[C_2^*]$ are the concentration of M_1-inserted and M_2-inserted active species, respectively. The ratio of Eqs. 1.41 and 1.42 gives the ratio of the two monomers incorporated in the copolymer:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[C_1^*][M_1] + k_{12}[C_1^{*]}[M_2]}{k_{21}[C_2^*][M_1] + k_{22}[C_2^*][M_2]} \tag{1.43}$$

The steady-state approximation is applied for $[C_1^*]$ and $[C_2^*]$ to give

$$k_{12}[C_1^*][M_2] = k_{21}[C_2^*][M_1] \tag{1.44}$$

or

$$\frac{[C_1^*]}{[C_2^*]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \tag{1.45}$$

Combining Eqs. 1.43 and 1.45 yields comonomer composition equation or copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \tag{1.46}$$

Here r_1 and r_2 are monomer reactivity ratios defined by Eqs. 1.47 and 1.48, indicating the relative activity of each monomer on the M_1-inserted and the M_2-inserted Ti species, respectively.

$$r_1 = \frac{k_{11}}{k_{12}} \tag{1.47}$$

$$r_2 = \frac{k_{22}}{k_{21}} \tag{1.48}$$

Substitute $[M_1]/[M_2]$ and $d[M_1]/d[M_2]$ with F and f in Eq. 1.46:

$$f = \frac{F(r_1 F + 1)}{F + r_2} \tag{1.49}$$

Rearrange Eq. 1.49 to give

$$\frac{F(f - 1)}{f} = \frac{r_1 F^2}{f} - r_2 \tag{1.50}$$

Thus, r_1 and r_2 can be evaluated from the slope and intercept of the $F(f-1)/f$ versus F^2/f plot in the copolymerization with various comonomer feed ratios. This method is known as a Finemann–Ross plot [23]. Since Eq. 1.50 is derived on condition that the copolymerization proceeds in a steady state, the conversion of each monomer should be kept low in order to determine the r_1 and r_2 values precisely with this method.

The values of r_1 and r_2 are the fundamental parameters for describing a copolymerization system, and hence characterizing the copolymerization ability of a catalyst. r_i is the ratio of two propagation rate constants involving M_i-inserted active species: the ratio always compares the propagation rate constant for the same monomer inserting the active species relative to the propagation rate constant for the other monomer. If $r_i > 1$, M_i-inserted active species preferentially inserts the same monomer M_i; if $r_i < 1$, M_i-inserted active species preferentially inserts the other monomer; if $r_i = 0$, M_i-inserted active species does not insert the same monomer. Thus, the product of monomer reactivity ratios, $r_1 \bullet r_2$, is indicative for the structure of the copolymer obtained: $r_1 \bullet r_2 > 1$, blocky; $r_1 \bullet r_2 = 1$, random; $r_1 \bullet r_2 = 0$, alternate.

1.4.2.2 Statistical Treatment

In Sect. 1.4.2.1, we noted that the nature of a steady-state copolymerization system is characterized by r_1 and r_2 which are determined from the comonomer compositions of copolymers [24]. The analysis of monomer sequence distribution in a copolymer gives more detailed information on the copolymerization because each monomer sequence reflects each propagation step.

We can analyze the comonomer composition and the monomer sequence distribution of a copolymer by a probabilistic method on the assumption that the copolymer is statistically stationary. In a binary copolymer which has high molecular weight enough to neglect the chain-end effects, any monomer unit possesses the preceding and succeeding monomer units (M_1 or M_2), and the probability that the mth monomer unit is a given monomer unit (M_1 or M_2) is independent of m and equal to the probability of the randomized monomer unit. When a copolymer satisfies these conditions, the sequence distribution of monomer is referred to as statistical stationarity. A certain limited length of monomer sequence also satisfies these conditions, and the following quantity can be defined.

$P_n\{M_iM_j...M_v\}$ = the probability that a randomized monomer sequence with n monomer units (n length) is a certain monomer sequence $M_iM_j...M_v(i,j,\ldots,v = 1 \text{ or } 2)$.

For example, possible sequences are as follows.

$n = 1$, M_1 and M_2;
$n = 2$, M_1M_1, M_1M_2, M_2M_1 and M_2M_2
$n = 3$, $M_1M_1M_1$, $M_1M_1M_2$, $M_1M_2M_1$, $M_1M_2M_2$, $M_2M_1M_1$, $M_2M_1M_2$, $M_2M_2M_1$ and $M_2M_2M_2$.

In general, 2^n kinds of sequences are present in the sequence with n length. According to the definition of $P_n\{M_iM_j...M_v\}$, $P_1\{M_i\}$, $P_2\{M_iM_j\}$ and $P_3\{M_iM_jM_k\}$ are the existence probabilities or mole fractions of the corresponding monomer, diad and triad, respectively.

For given n, the summation of the probabilities of all the possible monomer sequences is unit. Thus,

$$P_1\{M_1\} + P_1\{M_2\} = 1 \tag{1.51}$$

$$P_2\{M_1M_1\} + P_2\{M_1M_2\} + P_2\{M_2M_1\} + P_2\{M_2M_2\} = 1 \tag{1.52}$$

If a certain monomer sequence with n length is defined as $S^{(n)}$,

$$\begin{aligned} P_n\left\{S^{(n)}\right\} &= P_{n+1}\left\{S^{(n)}M_1\right\} + P_{n+1}\left\{S^{(n)}M_2\right\} \\ &= P_{n+1}\left\{M_1S^{(n)}\right\} + P_{n+1}\left\{M_2S^{(n)}\right\} \end{aligned} \tag{1.53}$$

In the case of $S^{(1)} = M_1$

$$P_1\{M_1\} = P_2\{M_1M_1\} + P_2\{M_1M_2\} = P_2\{M_1M_1\} + P_2\{M_2M_1\} \tag{1.54}$$

Thus,

$$P_2\{M_1M_2\} = P_2\{M_2M_1\} \tag{1.55}$$

Equation 1.55 corresponds to the steady-state approximation in the kinetic treatment, Eq. 1.44.

Generally, the substitution of $S^{(n)} = M_i^n$ for an arbitrary integer $n \geq 1$ in Eq. 1.53 yields:

$$\begin{aligned} P_{n+1}\{M_1^nM_2\} &= P_{n+1}\{M_2M_1^n\} \\ P_{n+1}\{M_2^nM_1\} &= P_{n+1}\{M_1M_2^n\} \end{aligned} \tag{1.56}$$

$P_2\{M_1M_2\}$ or $P_2\{M_2M_1\}$ is developed with Eq. 1.53 as follows:

$$\begin{aligned} P_2\{M_2M_1\} &= P_3\{M_2M_1M_2\} + P_3\{M_2M_1M_1\} \\ &= P_3\{M_2M_1M_2\} + P_4\{M_2M_1M_1M_2\} + P_4\{M_2M_1M_1M_1\} \\ &= \cdots \\ &= \sum_{n=1}^{\infty} P_n + 2\{M_2M_1^nM_2\} + \lim_{n\to\infty} P_{n+2}\{M_2M_1^{n+1}\} \end{aligned} \tag{1.57}$$

Since the second term is zero, the following equation is obtained.

$$\begin{aligned} P_2\{M_1M_2\} &= P_2\{M_2M_1\} \\ &= \sum_{n=1}^{\infty} P_{n+2}\{M_2M_1^nM_2\} + \sum_{n=1}^{\infty} P_{n+2}\{M_1M_2^nM_1\} \end{aligned} \tag{1.58}$$

$P_{n+2}\{M_2M_1^nM_2\}$ (or $P_{n+2}\{M_1M_2^nM_1\}$) is the existence probability of the M_1 (or M_2) homo sequence with n length, which is named as "run with n length" according to Harwood and Ritchey [25]. Equation 1.58 implies that $P_2\{M_1M_2\}$ or $P_2\{M_2M_1\}$ equals to the number fraction of total M_1 run or total M_2 run. We can understand this relation intuitively from the statistical stationarity of copolymer: an infinite number of M_1 run and M_2 run are alternatively connected with M_1M_2 and M_2M_1 diads.

$P_2\{M_1M_2\}$ and $P_2\{M_2M_1\}$ are the important quantities which characterize monomer sequence distribution in copolymer. Run number R is defined as a summation of the total number of run per 100 monomer units. That is:

$$R = 100(P_2\{M_1M_2\} + P_2\{M_2M_1\}) = 200P_2\{M_1M_2\} = 200P_2\{M_2M_1\} \tag{1.59}$$

Since M_1M_2 and M_2M_1 cannot be distinguished in vinyl polymers and $P_2\{M_1M_2\} = P_2\{M_2M_1\}$ under the stationary conditions, M_1M_2 represents the both hetero diads. It should be noted that all the equations containing $P_2\{M_1M_2\}$ or $P_2\{M_2M_1\}$ in this chapter is true by dividing those value by 2 for vinyl polymers.

1.4.2.3 Monomer Sequence Distribution and Copolymerization Mechanism

For simplicity, we postulate the conditions that monomer concentration, comonomer composition and monomer sequence distribution are practically constant [24]. When the diad probability of a certain copolymer is given, the number-average length of M_1 run (l_1) or M_2 run (l_2) can be calculated irrespective of the copolymerization mechanism:

$$l_1 = P_1\{M_1\}/P_2\{M_1M_2\} = 200P_1\{M_1\}/R \tag{1.60}$$

$$l_2 = P_1\{M_2\}/P_2\{M_2M_1\} = 200P_1\{M_2\}/R \tag{1.61}$$

When M_1 and M_2 are independently (or perfectly randomly) distributed, it is said that the distribution of M_1 and M_2 obeys Bernoulli trials, where the following relation is satisfied: $P_2\{M_1M_2\} = P_2\{M_2M_1\} = P_1\{M_1\}\,P_2\{M_2\}$; thus, $l_{1,\text{ random}} = 1/P_1\{M_2\}$, $l_{2,\text{ random}} = 1/P_1\{M_1\}$, $R_{\text{random}} = 200\ P_1\{M_1\}\ P_1\{M_2\}$. Persistence ratio ρ for a parameter characterizing the block nature of a given copolymer is defined by the following equation [26]:

$$\rho = \frac{R_{\text{random}}}{R} = \frac{l_1}{l_{1,\text{ random}}} = \frac{l_2}{l_{2,\text{ random}}} = \frac{2P_1\{M_1\}P_1\{M_2\}}{P_2\{M_1M_2\} + P_2\{M_2M_1\}} \tag{1.62}$$

It is apparent that $\rho = 1$ indicates Bernoulli trials, and $\rho > 1$ or $\rho < 1$ imply more blocky or more alternating than Bernoulli trials, respectively.

In general, when the probability that a certain monomer unit or a certain monomer sequence distribution occurs is dependent of the preceding N monomer units but independent of further preceding monomer units ($N + 1$ or more), the probability process is said to obey Nth-order Markov chain: $N = 0$ is equal to Bernoulli trials. First-order Markov chain ($N = 1$) is also called simple Markov chain. In Nth-order Markovian process, any monomer sequence $S^{(n)}$ satisfies the following equation:

$$\frac{P_{m+N+n}\{U^{(m)}V^{(N)}S^{(n)}\}}{P_{m+N}\{U^{(m)}V^{(N)}\}} = \frac{P_{N+n}\{V^{(N)}S^{(n)}\}}{P_{m+N}\{V^{(N)}\}} \tag{1.63}$$

Here, $V^{(N)}$ is the monomer sequence preceding $S^{(n)}$ with N length, and $U^{(m)}$ is any monomer sequence preceding $V^{(N)}$ with m length. The right-hand side of Eq. 1.63 is the conditional probability that monomer sequence $S^{(n)}$ occurs after a given monomer sequence $V^{(N)}$. Similarly, the left-hand side Eq. 1.63 is the conditional probability that monomer sequence $S^{(n)}$ occurs after a given monomer sequence $U^{(m)}V^{(N)}$. When the integer N which satisfies Eq. 1.63 does not exist, the probability process is said to be non-Malkov chain.

In order to correlate monomer sequence distribution with copolymerization mechanism, we define the conditional probability $P_{ijk\ldots\text{ vw}}$ ($i, j, k, \ldots, v, w = 1$ or 2) that the monomer unit M_w occurs after the monomer sequence $M_iM_j\ldots M_v$ in Nth-order Markov chain ($N \geq 0$).

$$P_{ijk\cdots vw} = \frac{P_{n+1}\{M_iM_jM_k\ldots M_vM_w\}}{P_n\{M_iM_jM_k\ldots M_v\}} \tag{1.64}$$

Since $M_w = M_1$ or M_2, Eqs. 1.53 and 1.64 give

$$P_{ijk\cdots v1} + P_{ijk\cdots v2} = 1 \tag{1.65}$$

The existence probability of a certain monomer sequence is expressed from Eq. 1.64:

$$\begin{aligned} &P_n\{M_iM_jM_k...M_uM_v\} \\ &= P_1\{M_i\}\cdot\frac{P_2\{M_iM_j\}}{P_1\{M_i\}}\cdot\frac{P_3\{M_iM_jM_k\}}{P_2\{M_iM_j\}}\cdot\cdots\cdot\frac{P_n\{M_iM_jM_k...M_uM_v\}}{P_{n-1}\{M_iM_jM_k...M_u\}} \\ &= P_1\{M_i\}P_{ij}P_{ijk}\cdots P_{ijk}\cdots \end{aligned} \tag{1.66}$$

Here, $P_1\{M_i\}$ is the probability that the randomly selected monomer unit is M_i; P_{ij}, P_{ijk} and $P_{ijk\ldots uv}$ are the conditional probabilities that M_j, M_k and M_v occur on condition that the preceding monomer sequences are $M_{i,}$ M_iM_j and M_iM_jjM_k…M_u, respectively. Equation 1.66 indicates that $P_\mathrm{n}\{M_iM_j$j$M_k\ldots M_v\}$ is given by the product of these n probabilities.

General Eq. 1.66 is simplified by deciding the N value of Nth-order Malkov chain according to a given copolymerization mechanism and can be calculated specifically. For example, the existence probability of the sequence of continuous n M_1 units, $P_{\mathrm{n}+2}\{M_2M_1^n\,M_2\}$ is calculated with a given N value:
when $N = 0$

$$\begin{aligned} &P_{n+2}\{M_2M_1^nM_2\} = (P_1\{M_2\})^2(P_1\{M_1\})^n = P_2^2P_1^n = (1-P_1)^2P_1^n \\ &(\because P_1\{M_1\} + P_1\{M_2\} = 1, P_1\{M_1\} = P_1, P_1\{M_2\} = P_2) \end{aligned} \tag{1.67a}$$

when $N = 1$

$$P_{n+2}\{M_2M_1^nM_2\} = P_1\{M_2\}P_{21}P_{11}^{n-1}P_{12} = P_2\{M_2M_1\}P_{11}^{n-1}P_{12} \tag{1.67b}$$

when $N = 2$

$$\begin{aligned} P_{n+2}\{M_2M_1^nM_2\} &= P_1\{M_2\}P_{21}P_{211}P_{111}^{n-2}P_{112} \\ &= P_2\{M_2M_1\}P_{211}^{n-1}P_{112}(n \geq 2) \end{aligned} \tag{1.67c}$$

$$P_3\{M_2M_1M_2\} = P_1\{M_2\}P_{21}P_{212} = P_2\{M_2M_1\}P_{212}(n = 1) \tag{1.67d}$$

The order of Malkov chain N can be experimentally evaluated by Eq. 1.63 when the existence probabilities at least with $N + 2$ length are independently given. The corresponding conditional probabilities can be directly obtained by Eq. 1.64 from the ratio of the existence probabilities of $N + 1$ length and N. The following relations are available when $N = 1$, 2, or 3, and i, j, k, $l = 1$ or 2:

when $N = 0$

$$\frac{P_2\{M_jM_i\}}{P_1\{M_j\}} = P_1\{M_i\} = P_i \tag{1.68a}$$

when $N = 1$

$$\frac{P_3\{M_kM_iM_j\}}{P_2\{M_kM_i\}} = \frac{P_2\{M_iM_{ij}\}}{P_1\{M_i\}} = P_{ij} \tag{1.68b}$$

when $N = 2$

$$\frac{P_4\{M_lM_iM_jM_k\}}{P_3\{M_lM_iM_j\}} = \frac{P_3\{M_iM_jM_k\}}{P_2\{M_iM_j\}} = P_{ijk} \tag{1.68c}$$

The copolymer of which monomer sequences do not satisfy these relations is Nth-order Malkov chain of $N \geq 3$ or non-Malkov chain.

Above discussion implies that we can fully characterize monomer sequence distribution of a given copolymer obtained with a low monomer conversion by the probabilistic method (without any kinetic parameter) if we can determine N of Malkov chain and all the existence probabilities of the monomer sequences with $N + 1$ length: the existence probabilities of monomer sequences below N length are determined by Eq. 1.53 and the conditional probabilities are determined by either Eq. 1.64 or 1.68a. Hereafter, we will take the copolymerization described in Sect. 1.4.2.1 as an example and consider how the conditional probabilities, comonomer composition and monomer sequence distribution are correlated with given kinetic parameters and monomer concentrations.

$$P_{12} = \frac{k_{12}[C_1^*][M_2]}{k_{11}[C_1^*][M_1] + k_{12}[C_1^*][M_2]} = \frac{1}{1 + r_1x} = 1 - P_{11} \tag{1.69a}$$

$$P_{21} = \frac{k_{21}[C_2^*][M_1]}{k_{22}[C_2^*][M_2] + k_{21}[C_2^*][M_1]} = \frac{1}{1 + r_2/x} = 1 - P_{22} \tag{1.69b}$$

Here, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $x = [M_1]/[M_2]$.

Copolymer composition equation is obtained from Eqs. 1.55 and 1.66:

$$P_1\{M_1\}P_{12} = P_1\{M_2\}P_{21}$$

thus,

$$P_1\{M_1\}/P_1\{M_2\} = P_{21}/P_{12} \tag{1.70a}$$

or from Eqs. 1.51 and 1.70a:

$$P_1\{\mathrm{M}_1\} = P_{21}/(P_{12} + P_{21}), P_1\{\mathrm{M}_2\} = P_{12}/(P_{12} + P_{21}) \tag{1.70b}$$

Substituting Eq. 1.69a, b, into Eq. 1.70a, we obtain comonomer composition equation (Eq. 1.46).

The existence probability of a certain monomer sequence is defined by P_{ij}. For example,

$$P_2\{\mathrm{M}_1\mathrm{M}_1\} = P_{21}P_{11}/(P_{12} + P_{21}) \tag{1.71a}$$

$$P_2\{\mathrm{M}_1\mathrm{M}_2\} = P_2\{\mathrm{M}_2\mathrm{M}_1\} = R/200 \ = P_{12}P_{21}/(P_{12} + P_{21}), \tag{1.71b}$$

$$P_2\{\mathrm{M}_2\mathrm{M}_2\} = P_{12}P_{22}/(P_{12} + P_{21}) \tag{1.71c}$$

$$P_3\{\mathrm{M}_1\mathrm{M}_1\mathrm{M}_1\} = P_{21}P_{11}^2/(P_{12} + P_{21}) \tag{1.71d}$$

$$P_3\{\mathrm{M}_1\mathrm{M}_1\mathrm{M}_2\} = P_3\{\mathrm{M}_2\mathrm{M}_1\mathrm{M}_1\} = P_{21}P_{11}P_{12}/(P_{12} + P_{21}) \tag{1.71e}$$

$$P_3\{\mathrm{M}_2\mathrm{M}_1\mathrm{M}_2\} = P_{21}P_{12}^2/(P_{12} + P_{21}) \tag{1.71f}$$

$$P_{n+1}\left\{\mathrm{M}_1^n\mathrm{M}_2\right\} = P_{n+1}\left\{\ \mathrm{M}_2\mathrm{M}_1^n\right\} = P_{21}P_{12}P_1^{n-1}\ {}_1/(P_{12} + P_{21}) \tag{1.71g}$$

Persistence ratio ρ and the number-average length of M_i are obtained similarly by substituting conditional probabilities into each definitional identity.

$$\rho = 1/(P_{12} + P_{21}) \tag{1.72}$$

$$l_1 = 1/P_{12},\ l_2 = 1/P_{21} \tag{1.72}$$

Equations 1.71a–1.73 are converted to the functions of monomer reactivity ratios and monomer feed ratio. For example,

$$R = 200/(2 + r_1x + r_2/x) \tag{1.73}$$

$$\rho = \frac{1 + r_1r_2 + r_1x + r_2/x}{2 + r_1x + r_2/x} \tag{1.74}$$

$$l_1 = 1 + r_1x,\ l_2 = 1 + r_2/x \tag{1.75}$$

Equation 1.74 shows the relation between ρ and the product of monomer reactivity ratios, $r_1 \bullet r_2$: $r_1 \bullet r_2 = 1$, $\rho = 1$ (Bernoulli trials); $r_1 \bullet r_2 > 1$, $\rho > 1$ (more blocky than Bernoulli trials); $r_1 \bullet r_2 < 1$, $\rho < 1$ (more alternate than Bernoulli trials).

When daid probabilities are experimentally obtained, l_1 and l_2 are directly obtained by Eq. 1.60. Thus, Eq. 1.75 is important for determining monomer reactivity ratios and testing terminal model by the linear plot against x or $1/x$. The direct evaluation of terminal model is to compare the probabilities of diad and triad which are experimentally obtained by Eq. 1.68b. For example,

$$\begin{aligned}\frac{P_3\{M_1M_1M_2\}}{P_2\{M_1M_1\}} &= \frac{P_3\{M_2M_1M_2\}}{P_2\{M_2M_1\}} = \frac{P_2\{M_1M_2\}}{P_1\{M_1\}} \\ &= P_{12} = \frac{1}{1+r_1x}\end{aligned} \tag{1.76}$$

If terminal model ($N = 1$) is confirmed, we can principally determine r_1 and r_2 from the diad probabilities of only one sample on condition that monomer feed ratio and comonomer composition are known.

$$\frac{P_2\{M1M1\}}{P_2\{M1M2\}} = \frac{k_{11}[C_1^*][M_1]}{k_{12}[C_1^*][M_2]} = r_1x \tag{1.77}$$

$$\frac{P_2\{M_2M_2\}}{P_2\{M_2M_1\}} = \frac{k_{22}[C_2^*][M_2]}{k_{21}[C_2^*][M_1]} = r_2/x \tag{1.78}$$

Since M_1M_2 and M_2M_1 cannot be distinguished in olefin copolymers, r_1 and r_2 is obtained by the following equations using a half of the observed $P_2\{M_1M_2\}$ (= $P_2\{M_1M_2\}$) as described in Sect. 1.4.2.2.

$$r_1 = \frac{P_2\{M_1M_1\}}{P_2\{M_1M_2\}\ /2} \cdot \frac{1}{x} \tag{1.80}$$

$$r_2 = \frac{P_2\{M_2M_2\}}{P_2\{M_1M_2\}\ /2} \cdot x \tag{1.81}$$

1.4.2.4 Comonomer Composition Distribution

A majority of LLDPE are still produced with $MgCl_2$-supported Ti-based catalysts, although a variety of single-site catalysts has been developed. As described in Sect. 1.3.4.3, $MgCl_2$-supported Ti-based catalysts contain a several active species which are different in isotactic-selectivity. We can imagine that these active species possess different selectivity also for the copolymerization of ethylene and 1-alkene. Since the crystallinity of LLDPE decreases inversely with the 1-alkene content, we can fractionate LLDPE by the difference of crystallinity. Figure 1.16a displays the cross fractionation chromatogram (CFC), which is obtained by a combination of TREF and gel permeation chromatography (GPC), of the ethylene–1-butene copolymer obtained with a Ti-based $MgCl_2$-supported catalyst, indicating that the copolymer contain several fractions differing in crystallinity and molecular weight. In contrast, Fig. 1.16b indicates that the copolymer obtained with a

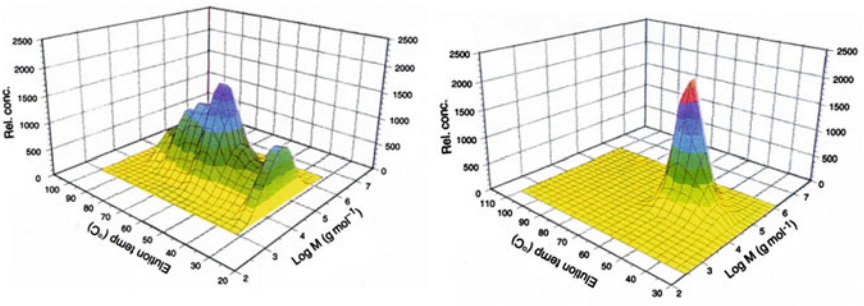


Fig. 1.16 CFC chromatograms of ethylene–1-butene copolymers obtained with **a** a heterogeneous Ziegler–Natta catalyst and **b** a homogeneous metallocene catalyst [27]

homogeneous metallocene catalyst is uniform both in molecular weight distribution and comonomer composition distribution.

In Sects. 1.4.2.1 and 1.4.2.3, we dealt with binary copolymerization with kinetic and probabilistic approaches, respectively, where we assume stationary conditions with one kind of active species. Thus, the methods are applied for single-site catalysts but not for multi-site catalysts. In the latter case, r_1 and r_2 obtained are apparent values.

1.5 Characteristics of Metallocene Catalysts

1.5.1 Activation Process of Metallocene

1.5.1.1 Active Species of Metallocene Catalyst

The research on Cp_2TiX_2–$R_nAlCl_{3\text{-}n}$ systems started from the 1950s [9]. Since the systems showed the low activity only for ethylene polymerization, these systems were investigated as a model for studying the polymerization mechanism. The epoch-making discovery of MAO as a cocatalyst for a metallocene complex by Kaminsky and Sinn has enabled a practical use of metallocenes for olefin polymerization catalysts [8]. Their first paper on ethylene polymerization is entitled "*Halogenfreie lösliche Ziegler-Katalysatoren für die Ethylen-Polymerisation. Regelung des Molekulargewichts durch Wahl der Reaktionstemperatur*", where Cp_2MMe_2 ($M = Ti, Zr$) was activated by the mixture of Me_3Al and H_2O [28]. Their finding is important also at the point that halogen, which had been believed to be indispensable to show high activity for olefin polymerization, is essentially unnecessary.

The research on a metallocene catalyst progressed rapidly both from the fundamental and practical point of views after the discovery. The study on Cp_2TiX_2–$R_nAlCl_{3\text{-}n}$ systems by a visible absorption spectrum, electrical conductivity,

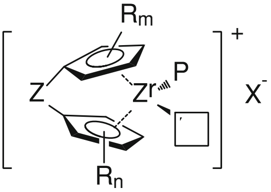


Fig. 1.17 Active species of group 4 metallocene catalyst

^{13}CNMR had presumed that the cationic Ti^{4+} species should be active for ethylene polymerization. Jordan et al. reported that the isolated cationic complex of Zr^{4+}, $[Cp_2ZrR(THF)][BPh_4](R = Me, CH_2Ph)$, conducted ethylene polymerization independently [29]. Furthermore, the formation of cationic Zr^{4+} species in a Cp_2ZrX_2–MAO system was confirmed by XPS [30] and solid CP MAS ^{13}CNMR [31]. It is no doubt that the active species of group 4 metallocene catalysts for olefin polymerization is coordinatively-unsaturated tetravalent alkyl cationic species (Fig. 1.17): the active species possesses a pseudo-tetrahedral structure where the bis(cyclopentadienyl) ligand of the precursor is retained and a growing polymer chain and a vacant site locate at *cis*-position. Namely, the structure of active species is determined by that of the metallocene precursor, which enables the molecular design of olefin polymerization catalysts.

1.5.1.2 Activation Method of Metallocene

It was considered that MAO should be necessary for metallocenes to show high activity in olefin polymerization [32]. The clarification of the active species has brought about various activation methods, which are classified as follows in the case of a dialkylmetallocene.

(1) One-electron oxidation

$$\begin{aligned}Cp_2ZrR_2 + \ Ag^+\left[B(C_6H_5)_4\right]^- \\ \rightarrow [Cp_2ZrR]^+\left[B(C_6H_5)_4\right]^- + 1/2R_2 + Ag^0\end{aligned} \tag{1.82}$$

$$\begin{aligned}Cp_2ZrR_2 + \left[(MeCp)_2Fe\right]^+\left[B(C_6H_5)_4\right]^- \\ \rightarrow [Cp_2ZrR]^+\left[B(C_6H_5)_4\right]^- + 1/2R_2 + (MeCp)_2Fe\end{aligned} \tag{1.83}$$

$$Cp_2ZrR_2 + [Ph_3C]^+\left[B(C_6F_5)_4\right]^- \rightarrow [Cp_2ZrR]^+\left[B(C_6F_5)_4\right]^- + Ph_3CR \tag{1.84}$$

(2) Protonolysis

$$\begin{aligned}&Cp_2ZrR_2 + [HNR_3]^+\left[B(C_6F_5)_4\right]^-\\&\quad\rightarrow [Cp_2ZrR]^+\left[B(C_6F_5)_4\right]^- + NR_3 + RH\end{aligned} \tag{1.85}$$

$$Cp_2ZrR_2 + \; ROH\cdot B(C_6F_5)_3 \rightarrow [Cp_2ZrR]^+[RO\cdot B(C_6F_5)_3]^- + RH \tag{1.86}$$

(3) Ligand abstraction

$$Cp_2ZrR_2 + B(C_6F_5)_3 \rightarrow \; [Cp_2ZrR]^+\left[RB(C_6F_5)_3\right]^- \tag{1.87}$$

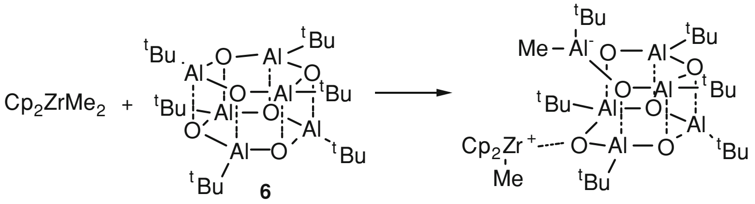
In order to form highly active and stable cationic species, the counter anion should be weakly coordinated to the cationic species and tolerant of the electrophilic attack by the cationic species. Thus, C_6F_5 group is selected and the high activity comparable to the MAO system is achieved by the use of $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $[PhNMe_2H]^+[B(C_6F_5)_4]^-$.

1.5.1.3 Structure and Role of MAO

MAO is a condensation product of Me_3Al and H_2O containing linear and cyclic oligomers with various degree of polymerization. Consequently the precise structure and activation process of MAO is not still clear. The structures of cyclic trimer (**1**) and linear tetramer (**2**) are shown in Fig. 1.18.

Sinn et al. proposed the spherical structure **4** composed of four linear tetramers which intramolecularly coordinate to form a cyclic structure, **3** [33]. The nano tube structure **5** with the same chemical composition with **4** is reported to be effective as a cocatalyst by quantum chemical calculation [34].

Barron et al. isolated a compound composed of two molecules of cyclic *tert*-butylaluminoxane trimer **6** and clarified that the distorted Al–O bond activated Cp_2ZrMe_2 as a potential Lewis acid site (Eq. 1.88) [35].



(1.88)

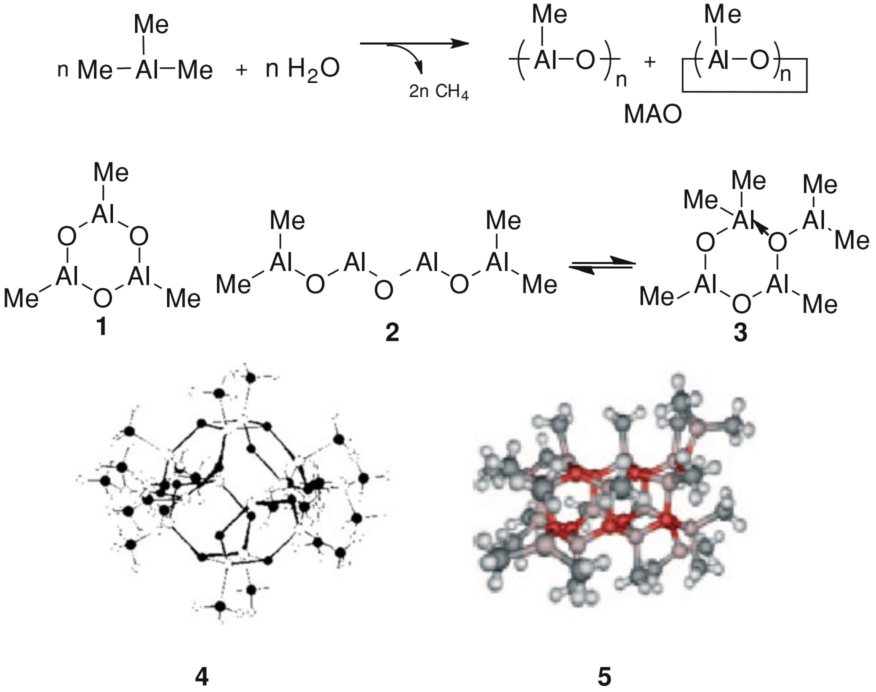


Fig. 1.18 Plausible structures of MAO [33, 34]

MAO contains free Me_3Al and acts as an alkylation reagent and a Lewis acid for the activation of metallocene dichloride (Eq. 1.89).

$$Cp_2ZrCl_2 \xrightarrow[\text{Me}_3\text{Al in MAO}]{} \left[Cp_2ZrMe_2 \right] \xrightarrow[\text{MAO}]{} [Cp_2ZrMe]^+ \; Me^- \; MAO \tag{1.89}$$

When the toluene solution of MAO is dried to remove free Me_3Al, the solubility of MAO is significantly decreased, indicating free Me_3Al donates the solubility of MAO. In order to increase the solubility of MAO, modified MAO (MMAO) is prepared from the mixture of Me_3Al and $^iBu_3Al$. MMAO is commercially available as toluene or hexane solution.

MAO and MMAO are also effective for the activation of various transition metal complexes such as Fe, Ni, Co to cause polymerization or oligomerization of olefins, where they should promote the formation of coordinatively unsaturated cationic metal–alkyl species similarly for group 4 metallocene.

1.5.1.4 Group 3 Metallocene

Trivalent group 3 metallocenes have a tendency to form dimer [36]. Mononuclear trivalent group 3 metallocene possessing hydride or alkyl group, which has the isoelectronic structure of group 4 tetravalent cationic metallocene, conducts polymerization of olefin [37, 38]. Binuclear samarocene hydride, $[(Me_5C_5)_2H]_2$, was dissociated to conduct syndiotactic-specific living polymerization of methyl methacrylate [39, 40]. Divalent samarocene was oxidized via one-electron transfer to monomer to form a binuclear initiator, which was applied for the synthesis of tri-block copolymers [41].

1.5.2 Tacticity Control of Polypropylene

Metallocene catalysts give various kinds of polypropylenes such as highly isotactic, highly syndiotactic, statistically atactic, hemi-isotactic or stereoblock, depending on the structure of bis(cyclopentadienyl) ligand [9]. In this section are explained the relation between the structure of metallocene and the mechanism of stereospecific polymerization.

1.5.2.1 C_{2v}-symmetric Metallocene

In achiral C_{2v}-symmetric metallocene, two coordination sites where monomer and propagation chain occupy are equivalent and the derived coordinatively-unsaturated cationic alkyl species is achiral except the chiral carbon of propagation chain-end. When the effect of the chiral carbon is negligible, atactic polymer is produced (Fig. 1.19).

Ewen investigated the effect of polymerization temperature on propylene polymerization with Cp_2TiPh_2–MAO [42]. The catalytic system gave statistically atactic polypropylene at 25 °C (Fig. 1.20a). The effect of the chain-end chiral carbon was not negligible at lower temperature where the rotation of $M–C–C^*$ bonds was suppressed to give isotactic polypropylene by a chain-end controlled mechanism (Fig. 1.20c).

1.5.2.2 *Ansa*-C_2-Symmetric Metallocene

Ansa-C_2-Symmetric metallocene possesses a pair of enantiomers. *rac*-$(CH_2)_2(Ind)_2ZrMe_2$ (**7a**) is shown in Fig. 1.21 as a representative of *ansa*-C_2-symmetric metallocene, where two coordination sites are equivalent and the same prochiral face of propylene is selected after the activation to produce isotactic polypropylene.

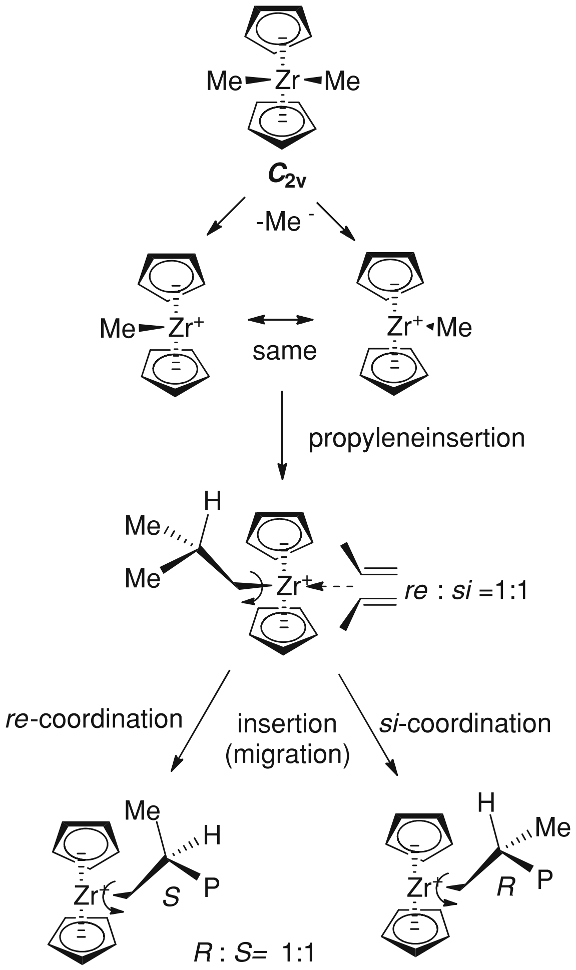


Fig. 1.19 Non-stereospecific polymerization with C_{2v}-symmetric metallocene

Pino et al. clarified how the prochiral face of propylene was selected by *ansa*-C_2-symmetric metallocene [44]. They resolved (−)-*R*-$(CH_2)_2(IndH_4)_2ZrMe_2$ (**8a**) and used it as a catalyst for propylene polymerization in the presence of hydrogen to obtain propylene oligomers. The configuration of the chiral chain-end carbons indicated the coordination state of propylene, where propylene coordinates to the Zr species in order to minimize the repulsion of its methyl group away from β-carbon of the propagation chain which is oriented by the chiral ligand structure (Fig. 1.22). The mechanism is basically the same with that in heterogeneous Ziegler–Natta catalysts proposed by Cossee and Arlman [45, 46] and investigated by Corradini et al. in detail [47].

The results of propylene polymerizations with representative C_2-symmetric metallocenes are summarized in Table 1.1. In *ansa*-bis(indenyl) derivatives, the

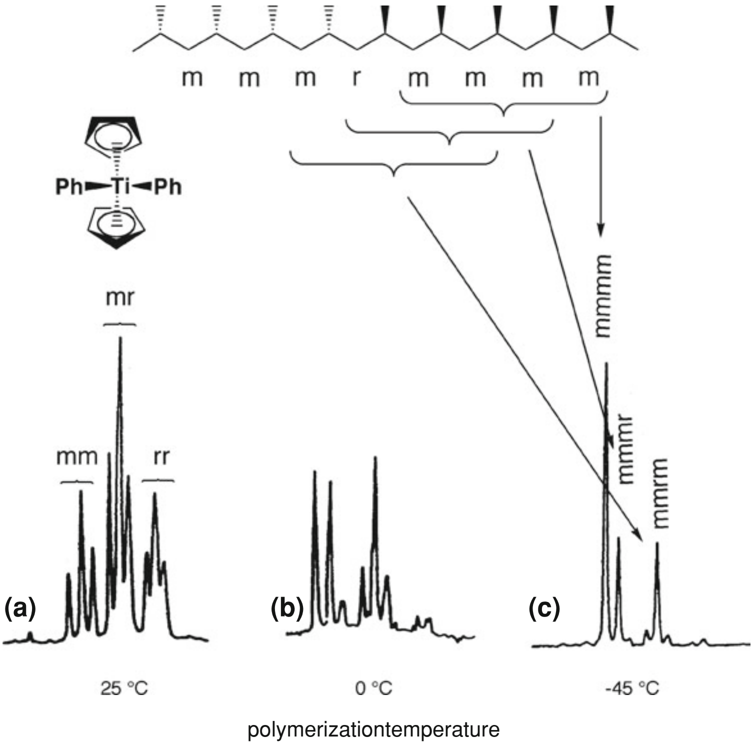


Fig. 1.20 Propylene polymerization with Cp_2TiPh_2–MAO [42]

introduction of bulky substituent at 4-position improved activity and mmmm value. The improvement of isotacticity is explained by the improvement of the selectivity of prochiral face according to the transition state shown in Fig. 1.22. The σ values determined from mmmm are also shown in Table 1.1. The highest σ value reached 0.998 in **14**, which gave the polymer with the melting point of 161 °C. Zirconocene **17** with lower σ values gave the polymers with higher melting points, which is ascribed to high regioselectivity compared with **14**. The rate enhancement should be ascribed to the prohibition of the counter anion coordination by the bulky substituent. The introduction of methyl group at 2-position increased the molecular weight of the polymer produced due to the suppression of chain transfer by monomer (see Sect. 1.5.3)

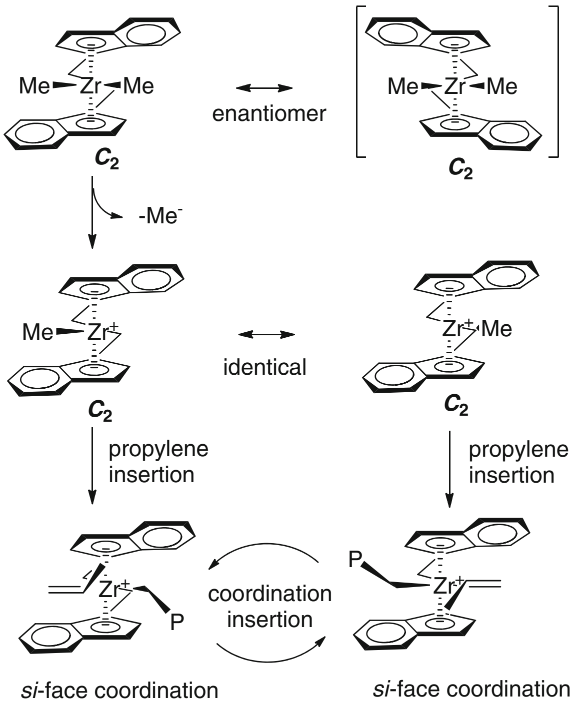


Fig. 1.21 Isotactic-specific polymerization with C_2-symmetric metallocene [43]

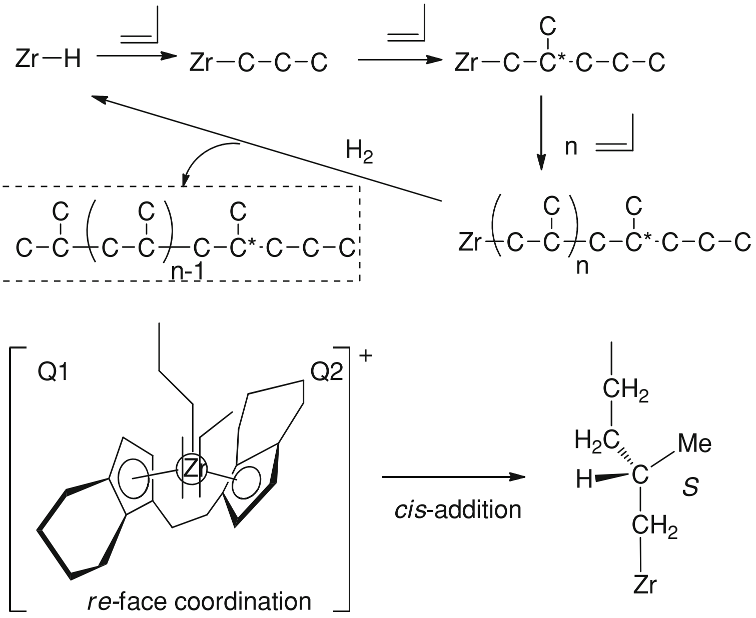


Fig. 1.22 Hydrooligomerization of propylene and its transition state with (−)-*R*-$(CH_2)_2(IndH_4)_2ZrMe_2$–MAO [44]

Table 1.1 Propylene polymerization with C_2-symmetric zirconocene–MAO

Complex[a]	Activity (kg PP/mmol-M/h)	$\bar{M}_{\mathrm{w}}$ ($\times 10^3$)	mmmm[b] (%)	σ[c]	T_{m}[d] (°C)	Refs.
7b[e]	188	24	78.5	0.952	132	[48]
8b[e]	80	15	–	–	125	[48]
9[e]	190	36	81.7	0.96	137	[49]
10[e]	99	195	88.5	0.976	145	[49]
11[e]	245	213	88.6	0.976	150	[49]
12[e]	403	330	88.7	0.976	146	[49]
13[e]	755	729	95.2	0.99	157	[49]
14[e]	875	920	99.1	0.998	161	[49]
15[f]	16.3	13.7	92.5	0.985	148	[50]
16[f]	11.1	86.5	97.1	0.994	160	[50]
17a[f]	1.59	134	97.7	0.995	162	[50]
17b[f]	0.3	256	98.7	0.997	163	[51]

[a] One of the enantiomers is illustrated

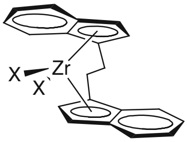
[b] Isotactic pentad

[c] Selectivity of prochiral face of propylene; $\sigma \approx \sqrt[5]{\mathrm{mmmm}}$

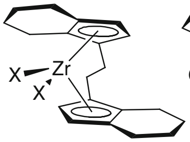
[d] Melting temperature

[e] Bulk polymerization, Al/M = 15000, 70 °C

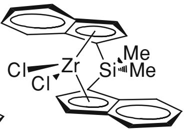
[f] Propylene = 3 kg/cm^2 G, toluene = 500 ml, Al/M = 10000, 30 °C



7a: X=Me, **7b**: X=Cl



8a: X=Me, **8b**: X=Cl



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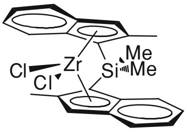

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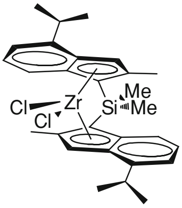

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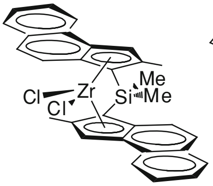

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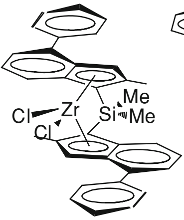

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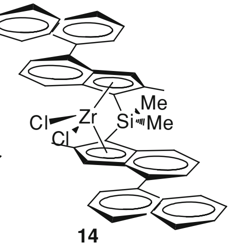

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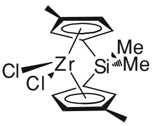

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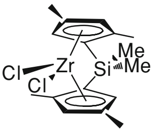

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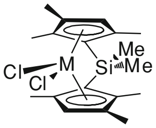


17a: M = Zr **17b**: M = Hf

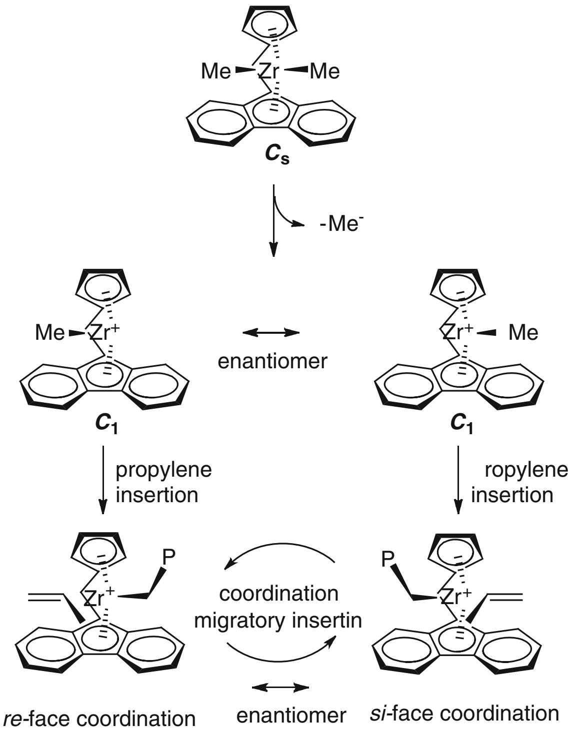


Fig. 1.23 Syndiotactic-specific polymerization with C_s-symmetric metallocene [52]

1.5.2.3 *Ansa*-C_s-Symmetric Metallocene

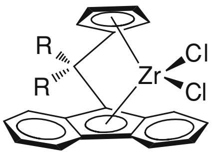
In *ansa*-C_s-symmetric metallocene, two coordination sites are enantiotopic and the activation of Me^- abstraction gives an enantiomeric pair of active species (Fig. 1.23). Since the propagation proceeds via the migration of the propagation chain, syndiotactic polypropylene is produced by the alternating coordination of *re* and *si* face of propylene on each site. In other words, the production of highly syndiotactic polypropylene with *ansa*-C_s-symmetric metallocene is the experimental evidence that the propagation proceeds via the migration of alkyl chain to the coordinated monomer. The synthesis of highly syndiotactic polypropylene has been realized for the first time by *ansa*-C_s-symmetric metallocene catalyst [52].

If we extend the coordination mode of propylene on the cationic C_2-symmetric metallocene shown in Fig. 1.22, the propagation chain is placed by the repulsion of the ligand and propylene coordinates the Zr species with minimizing the repulsion to the propagation chain.

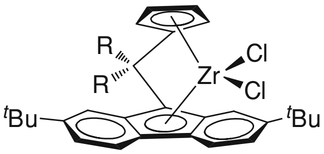
The results of propylene polymerizations with representative C_s-symmetric metallocenes are summarized in Table 1.2.

Table 1.2 Propylene polymerization with C_s-symmetric zirconocene–MAO

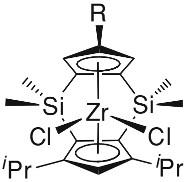
Complex	Temp. (°C)	Activity (kg PP/mmol-Zr/h)	$\bar{M}_w$ (× 10^3)	rrrr[a]	T_m^b (°C)	Refs.
18a	60	435	90	82	137	[52]
18b	60	251	200	88.8	140	[53]
19a	60	152	79	–	134	[54]
19b	60	598	172	–	137	[54]
20a	20	255	1250	93.4	151	[55]
20a	50	721	330	90.6	138	[55]
20b	20	29	980	97.5	151	[55]



18a: R = Me
18b: R = Ph



19a: R = Me
19b: R = Ph



20a: R = H
20b: R = ^{i}Pr

1.5.2.4 *Ansa*-C_1-Symmetric Metallocene

In *ansa*-C_1-symmetric metallocene, two coordination sites are non-equivalent and the selectivity of the prochiral face of propylene is alternating changed if the propagation proceeds via chain-migratory insertion. When methyl group was introduced at the 3-position of Cp ligand in **18a**, hemiisotactic polypropylene was produced due to the following mechanism. When the propagation chain is located at the methyl-substituted side, the position of the propagation chain cannot be fixed because of the similar steric effect of the methyl and the fluorenyl group to cause no selectivity of the prochiral face of propylene (Fig. 1.24).

When *tert*-butyl group was introduced at the 3-position of Cp ligand in **18b**, isotactic polypropylene was produced. The formation of isotactic polymer is explained by a chain stationary mechanism: the propagation chain cannot be located at the *tert*-butyl-substituted side because of the steric repulsion and always stays at the non-substituted site where the position of the propagation chain can be fixed to select the same prochiral face of propylene (Fig. 1.25).

The relation between the structure of *ansa*-C_1-symmetric zirconocene and the isotactic triad of the obtained polypropylene is shown in Fig. 1.26. Highly isotactic polypropylene was obtained with **24**. *ansa*-C_1-symmetric metallocene such as **21** and **25** has an advantage in the catalyst synthesis compared with C_2-symmetric metallocene and C_1-symmetric metallocene like **22**–**24**: the former gives only an enantiomeric pair, whereas the latter gives a meso form or diastereomers as byproduct.

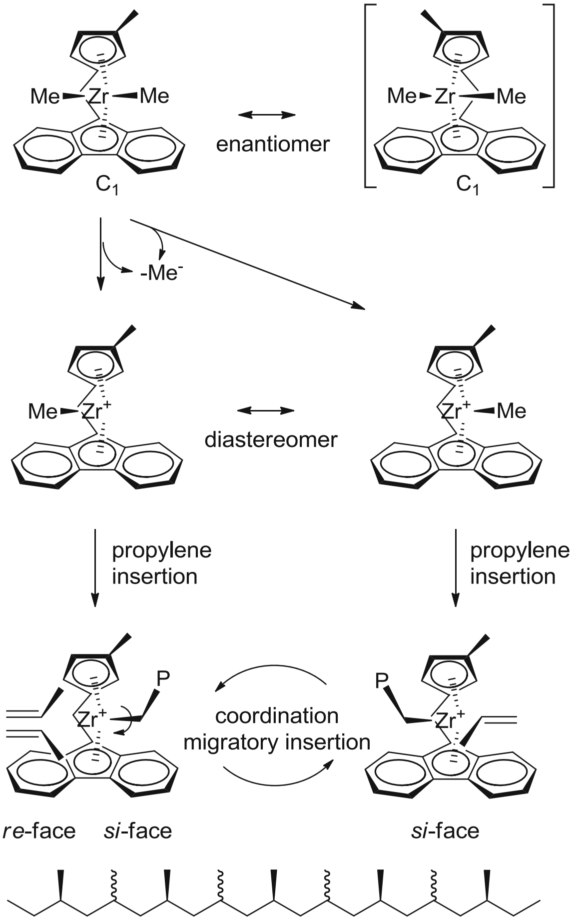


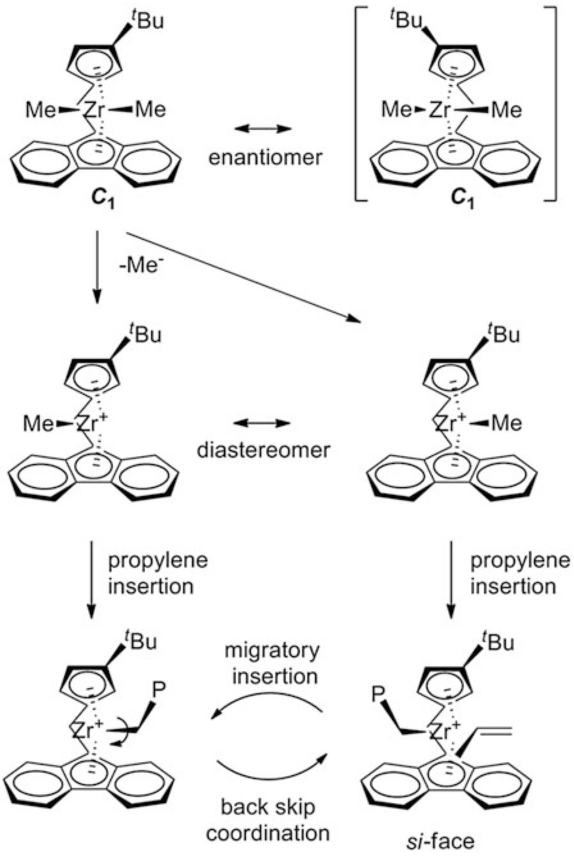
Fig. 1.24 Hemiisotactic-specific polymerization with C_1-symmetric metallocene [56, 57]

1.5.2.5 Stereoblock Polypropylene

Natta obtained stereoblock polypropylene composed of isotactic and atactic segments by the solvent extraction of the polypropylene produced by $TiCl_4$–Et_3Al [61]. The polypropylene showed elastic behavior because of the physical cross-linkage formed by the crystallization of the isotactic segments.

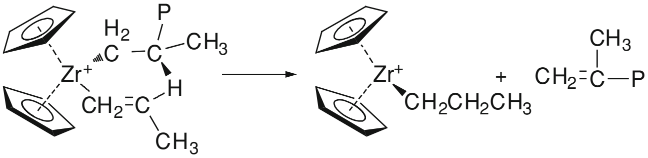
Stereoblock polypropylene was obtained also by *ansa*-C_1-symmetric titanocene [62] and bis(indenyl)zirconocene derivative [63], where the active species reversibly isomerizes between non-stereospecific and isotactic-specific during chain propagation according to the mechanism shown in Fig. 1.27a, b, respectively.

Fig. 1.25 Isotactic-specific polymerization with C_1-symmetric metallocene [56, 57]



1.5.3 Control of Chain Transfer Reaction

In propylene polymerization or copolymerization of ethylene and propylene with Cp_2ZrCl_2-MAO or *rac*-$(CH_2)_2(H_4Ind)_2ZrCl_2$-MAO, β-hydrogen transfer to monomer or to the metal center at the propylene-inserted chain end is predominant to form vinylidene-terminated polymers (Eqs. 1.90 and 1.91).



(1.90)

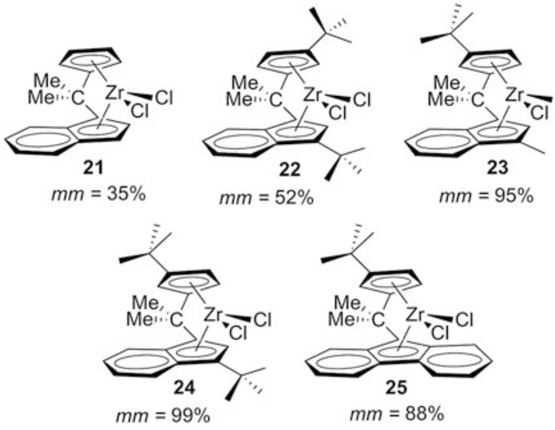


Fig. 1.26 Structure of *ansa*-C_1-symmetric metallocene and isotactic triad of polypropylene obtained [58–60]

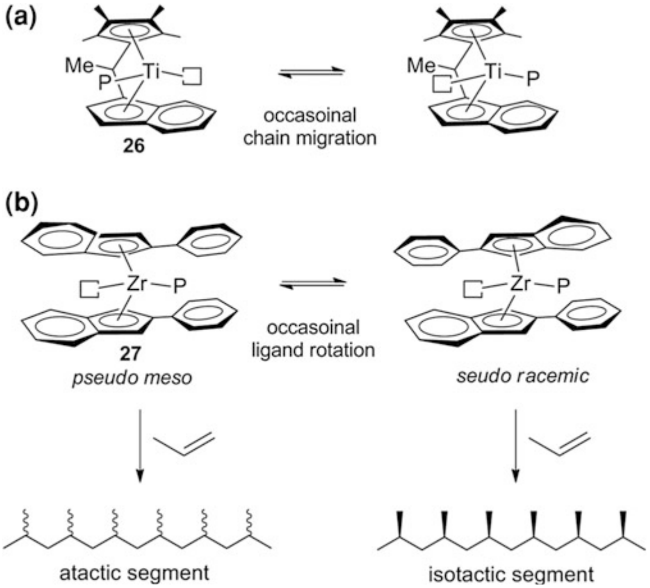
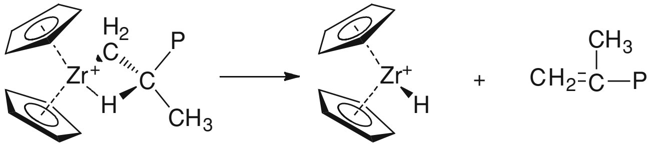
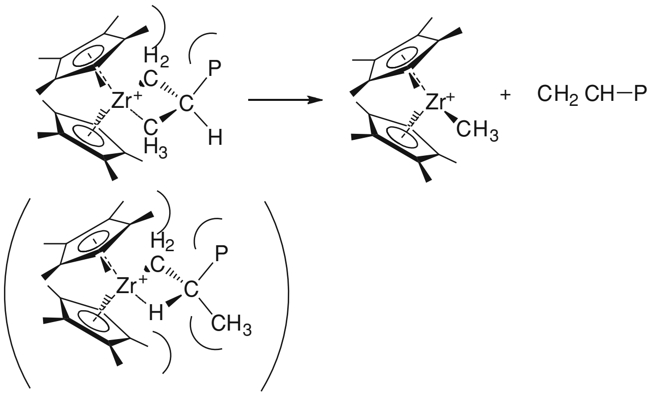


Fig. 1.27 Formation of stereoblock polypropylene by metallocene catalysts: **a** *ansa*-C_1 symmetric titanocene [62], **b** bis(2-phenylindenyl)zirconium derivative [63]



(1.91)

When a hindered metallocene such as $(C_5Me_5)_2ZrCl_2$ is used, β-methyl transfer to the metal center occurs predominantly to give vinyl-terminated polypropylene due to the steric repulsion of the transition state (Eq. 1.92) [64–66].



(1.92)

It was considered that chain transfer to coordinated monomer should not be inevitable in olefin polymerization because it is competitive with propagation reaction. However, the introduction of methyl group at 2-position in C_2-symmetric *ansa*-bis(indenyl)zirconocene derivatives was found to suppress chain transfer to monomer to produce high molecular-weight isotactic polypropylene: the steric repulsion of the methyl group prohibits the 6-membered transition state of the chain transfer as shown in Fig. 1.28.

1.5.4 Copolymerization of Olefins

Copolymerization of olefins is very important from the practical point of views. Metallocene catalysts are very important in this field because they copolymerize various olefins in high activity to give uniform copolymers.

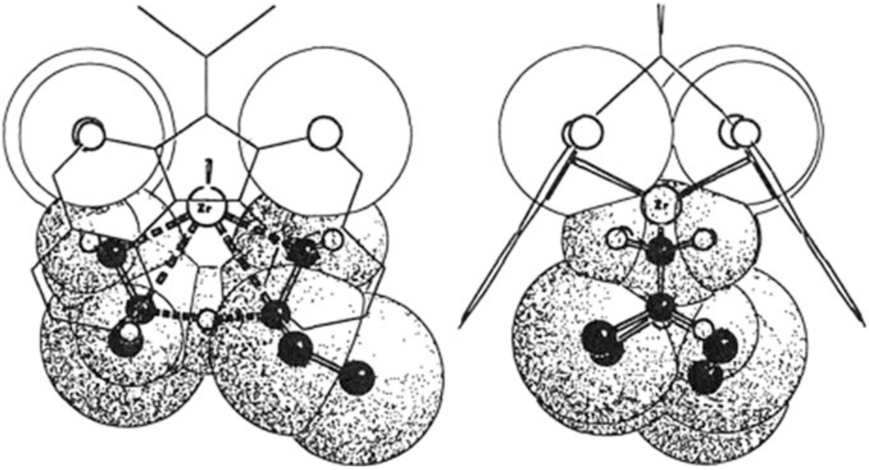


Fig. 1.28 Prohibition of chain transfer to monomer with a sterically-hindered C_2-symmetric metallocene, **11** [49]

1.5.4.1 Copolymerization of Ethylene and 1-Alkene

The majority of LLDPE are produced by highly active $MgCl_2$-supported Ti-based catalysts. However, LLDPE produced by metallocene catalysts has begun to gain share because of its excellent physical properties. Table 1.3 shows the monomer reactivity ratios of ethylene-1-alkene copolymerization with typical metallocene catalysts and those with heterogeneous Ziegler–Natta catalysts for reference.

The $r_E \bullet r_{1\text{-}A}$ values of the metallocene catalysts are approximately one or less regardless of the comonomer employed, indicating random or alternating tendency of these catalytic systems. The r_E values of *ansa*-bis(indenyl) and *ansa*-(cyclopentadienyl)(fluorenyl) derivatives are lower than that of Cp_2ZrCl_2, indicating better copolymerization ability for 1-alkene.

On the other hand, the $r_E \bullet r_{1\text{-}A}$ values of the conventional heterogeneous catalysts are more than one, suggesting the block tendency of the copolymerization. The $r_E \bullet r_{1\text{-}A}$ value of ethylene–1-butene $TiCl_4/MgCl_2$ was reported to be 1.14, suggesting random copolymerization. However, the copolymer obtained was fractionated by diisopropyl ether, hexane and cyclohexane into five parts, and the r_E and r_{1-A} values of each fraction determined by Eqs. 1.80 and 1.81 were found to vary from 12 to 1 and from 0.1 to 1.1, respectively [72]. The result indicates the presence of multiple active species with different copolymerization ability.

1.5.4.2 Copolymerization of Ethylene and Propylene

EPR and ethylene-propylene-diene terpolymer (EPDM) have been produced by V-based homogeneous Ziegler–Natta catalysts. Metallocene catalysts can be applied

Table 1.3 Monomer reactivity ratios in copolymerization of ethylene and 1-alkene

Catalyst[c]	1-alkene	Temp. (°C)	r_E^a	r_{1-A}^b	$r_E \bullet r_{1-A}$	Refs.
Cp_2ZrCl_2–MAO	1-butene	40	55	0.02	1.10	[67]
Cp_2ZrCl_2–MAO	1-butene	60	65	0.01	0.65	[67]
Cp_2ZrCl_2–MAO	1-butene	80	85	0.01	0.85	[67]
Cp_2ZrCl_2–MAO	1-butene	85	125	0.01	1.25	[67]
Cp_2ZrCl_2–MAO	1-hexene	60	62.3	0.003	0.19	[68]
$(Ind)_2ZrCl_2$–MAO	1-hexene	60	88.0	0.005	0.44	[68]
7b–MAO	1-hexene	60	31.0	0.013	0.40	[68]
8b–MAO	1-hexene	40	12.1	0.028	0.34	[69]
9–MAO	1-octene	40	18.9	0.014	0.26	[70]
10–MAO	1-octene	40	19.5	0.013	0.25	[70]
12–MAO	1-octene	40	10.1	0.118	1.19	[70]
18a–MAO	1-hexene	40	5.7	0.05	0.29	[69]
7b–MAO	4-methyl-1-pentene	40	50	0.004	0.20	[71]
$TiCl_4/MgCl_2$–$AlEt_3$	1-butene	80	3.17	0.36	1.14	[72]
$TiCl_3/MgCl_2$–$AlEt_3$	1-hexene	40	21	0.069	1.45	[73]
Solvay $TiCl_3^c$	1-butene	40	69	0.058	4.00	[74]
Solvay $TiCl_3^c$	1-hexene	40	69	0.033	2.28	[74]
Solvay $TiCl^c$	4-methyl-1-pentene	40	150	0.034	5.10	[74]

[a] Reactivity ratio of ethylene
[b] Reactivity ratio of 1-alkene
[c] Cp_2TiMe_2 was used as a cocatalyst

for the production of these copolymers. Table 1.4 summarizes the monomer reactivity ratios of ethylene–propylene copolymerization with typical metallocene catalysts and those with conventional homogeneous and heterogeneous Ziegler–Natta catalysts.

The $r_E \bullet r_P$ values of V-based homogeneous catalysts are approximately 0.2, indicating alternating tendency of the catalytic systems, although the catalysts need low temperature to form uniform active species. The $r_E \bullet r_P$ values of metallocene catalysts are less than one and scattered depending on the metallocene ligand. In the case of Ti-based heterogeneous catalysts, the monomer reactivity ratios, r_E and r_P, are the average of those of multiple active species, and the $r_E \bullet r_P$ values are approximately two.

Alternating copolymers of ethylene (M_1) and a bulky olefin (M_2) such as isobutene or norbornene are obtained due to the large difference in the polymerization ability between M_1-inserted and M_2-inserted active species. The most typical case is the catalyst that cannot conduct homopolymerization of M_2: poly (M_1-*alt*-M_2) is obtained in the presence of excess M_2. Since olefin polymerization with metallocene catalysts basically proceeds via chain migration to the coordinated monomer, the reactivity of the active species alternating changes in each propagation step if two coordination site of metallocene are non-equivalent such as *ansa*-*meso*-bis(indenyl) or C_1-symmetric metallocenes.

Selecting a suitable metallocene and polymerization conditions, we can synthesize poly(ethylene-*alt*-propylene) as shown in Table 1.5.

Table 1.4 Monomer reactivity ratios in copolymerization of ethylene and propylene

Catalyst[c]	Temp. (°C)	r_{E}[a]	r_{P}[b]	$r_{\mathrm{E}} \bullet r_{\mathrm{P}}$	Refs.
Cp_2ZrMe_2–MAO	60	31.5	0.005	0.16	[75]
Cp_2ZrCl_2–MAO	50	16.1	0.033	0.53	[76]
Cp_2ZrCl_2–MAO	40	48	0.015	0.72	[73]
$(Me_5Cp)_2ZrCl_2$–MAO	50	250	0.002	0.50	[76]
Cp_2TiPh_2–MAO	50	19.5	0.015	0.29	[76]
7b–MAO	50	6.61	0.06	0.40	[77]
7b–MAO	25	6.26	0.11	0.69	[77]
8b–MAO	40	11.6	0.084	0.97	[73]
18a–MAO	25	1.3	0.2	0.26	[78]
18a–MAO	40	7.0	0.072	0.50	[73]
VCl_4–$AlEt_3$	30	10.3	0.025	0.26	[79]
$VOCl_3$–Et_2AlCl	30	12.1	0.018	0.22	[79]
$VO(OBu)_3$–Et_2AlCl	30	19.8	0.012	0.24	[79]
TCl_3– $(hexyl)_3Al$	75	15.72	0.110	1.73	[80]
AA $TiCl_3$–Et_2AlCl	70	11.6	0.35	4.06	[81]
Solvay $TiCl_3$–Cp_2TiMe_2	40	10	0.22	2.20	[74]
$TiCl_3$–Et_3Al	40	9.02	0.21	1.89	[73]
$TiCl_4/MgCl_2$/EB–Et_3Al/EB[d]	70	5.5	0.36	1.98	[81]
$TiCl_4/MgCl_2$/2EHA–Et_2AlCl[e]	90	6.0	0.02	0.12	[81]

[a] Reactivity ratio of ethylene

[b] Reactivity ratio of propylene

[c] Metallocenes were activated by MAO

[d] EB, ethyl benzoate

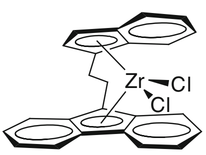
[e] Heptane-soluble system where $MgCl_2$ dissolved in 2-ethylhexan-1-ol (2EHA) was added

Table 1.5 Alternating copolymerization of ethylene and propylene with zirconocene activated by MAO

Zr	E/P[a]	Temp.(°C)	Activity[b]	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w/\bar{M}_n$	[EPE] + [PEP] (%)	Refs.
28	1/20	−40	11	3.1	2.1	93	[82]
29	1/9	0	7130	17.6	2	73	[83]
30	1/13	0	–	–	–	77	[83]
31a	1/30	0	20500	12.3	2	84	[84]
31b	1/50	0	20000	293	3.1	89	[84]
32a	1/9	0	480	14.9[b]	–	86	[84]
32b	1/9	0	1540	22.4[b]	–	85	[84]

[a] Molar ratio of ethylene and propylene

[b] kg/mmol-Zr/h



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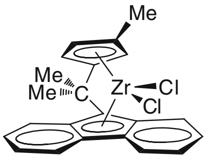

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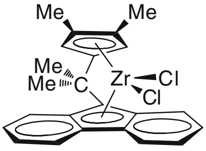

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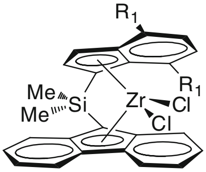
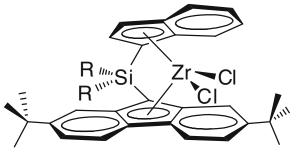


31a: R_1 = H, R_2 = H
31b: R_1 = H, R_2 = Me



32a: R = Me
32b: R = Ph

The mechanisms of the production of poly(ethylene-*alt*-propylene) with C_1-symmetric and C_s-symmetric metallocene are illustrated in Fig. 1.29, where the bulky ligand environment or the bulky chain-end formed by propylene insertion prohibits the coordination of next propylene. The mechanisms correspond to those of stereospecific polymerization of propylene, i.e., catalyst-site control or chain-end control. Figure 1.29a indicates that copolymerization with C_1-symmetric metallocene cannot be analyzed by first-order Malkovian process or a simple terminal model [83, 85].

It is difficult for us to synthesize block copolymers composed of ethylene and propylene by the use of metallocene catalysts because of their poor living polymerization character for both ethylene and propylene. Block copolymers composed of polypropylene and EPR segments were synthesized by $V(acac)_3$–Et_2AlCl, although the polypropylene segment was not crystallized due to the low stereoregularity (rr $\approx$ 65 %) [86]. Development of post-metallocene catalysts have realized living or controlled polymerization of ethylene, propylene and other olefins, which enables us to synthesize various olefin block copolymers possessing the melting points of polyethylene and/or stereoregular polypropylenes [87].

1.5.4.3 Copolymerization of Ethylene and Norbornene

Cycloolefin polymer (COP) and cyclic olefin copolymer (COC), which consist of rigid alicyclic polymer-backbone, are attractive materials because of their good heat and chemical resistance as well as their low dielectric constants, nonhygroscopicity, and high transparency [88]. COP is synthesized via ring-opening metathesis polymerization (ROMP) of norbornene derivatives followed by hydrogenation of C=C bonds in main chain [89, 90], whereas COC via copolymerization of ethylene and cycloolefin such as norbornene.

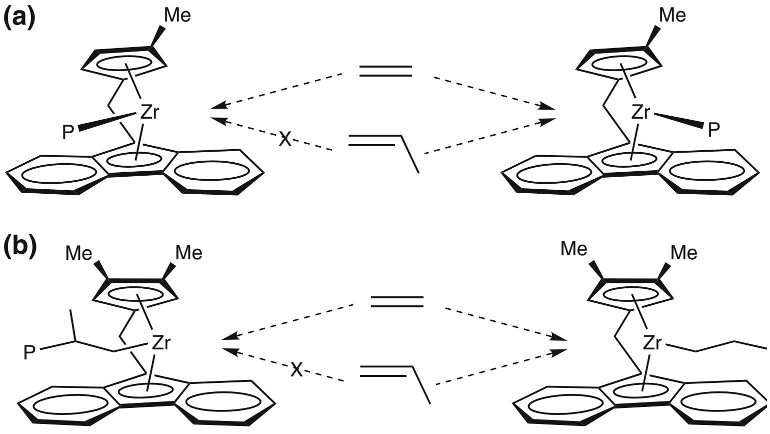


Fig. 1.29 Alternating copolymerization of ethylene and propylene with C_1-symmetric (**a**) and C_s-symmetric (**b**) metallocenes [83]

Table 1.6 Monomer reactivity ratios in copolymerization of ethylene and norbornene[a]

Zr	Symmetry	Temp (°C)	r_E^b	r_N^b	$r_E \bullet r_N$	Refs.
Cp_2ZrCl_2	C_{2v}	23	20	<0.1	≈1	[91]
8b	C_2	25	6	0.10	0.7	[91]
9	C_2	30	2.6	<1	≈1	[92]
18a	C_s	30	3.4	0.06	0.2	[92]
18b	C_s	30	3.0	0.05	0.15	[92]
25	C_1	30	3.1	0	0	[92]

[a] Cocatalyst, MAO

[b] r_E and r_N, monomer reactivity ratios of ethylene and norbornene, respectively

Efficient copolymerization of ethylene and norbornene has been achieved by metallocene catalysts. The comonomer sequence of ethylene–norbornene copolymer can be controlled by the metallocene used similarly to ethylene–propylene copolymer described in Sect. 1.5.4.2. Monomer reactivity ratios of typical zirconocenes in copolymerization of ethylene and norbornene are summarized in Table 1.6.

1.6 Conclusion

Development of metallocene catalysts has brought us fruits both in a fundamental and a practical point of view. Metallocene catalysts clarified the mechanism of coordination polymerization of olefins, which had been estimated from the intensive study on heterogeneous Ziegler–Natta catalysts, owing to the well-characterized active species. Metallocene catalysts have realized the production of uniform copolymers of olefins such as LLDPE, EPR, and COC in high activity. The random copolymerization of ethylene and styrene was also achieved by an *ansa*-zirconocene compound [92].

Of course, metallocene catalyst is not a panacea for coordination polymerization. So-called post-metallocene catalysts as well as half metallocene catalyst have therefore been developed for living polymerization of olefins, stereospecific homo- and copolymerization of styrene and conjugated diolefin, copolymerization of olefin and polar monomer and so on. These topics will be described in the following chapters in detail.

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Chapter 2
Olefin Polymerization with Half-Metallocene Catalysts

Kotohiro Nomura and Jingyu Liu

Abstract In this chapter, recent development of half-sandwich titanium complexes containing anionic donor ligands as the catalyst precursors for olefin polymerization has been described. These catalysts display unique characteristics especially for synthesis of new ethylene copolymers by incorporation of new monomers that are very difficult or impossible to be incorporated in ethylene copolymerization by conventional Ziegler-Natta and ordinary metallocene catalysts. Both cyclopentadienyl fragment and anionic donor ligand play an essential key role for both the catalytic activity and the comonomer incorporation in the copolymerization.

2.1 Introduction

Polyolefins such as polyethylene [high density polyethylene (HDPE), linear low density polyethylene (LLDPE) etc.], polypropylene, produced by metal catalyzed olefin coordination polymerization, are important commercial synthetic polymers in our daily life, and the market capacity still increases every year [1–3]. Recently, considerable attention has been paid to produce new polymers with specified functions exemplified by COCs (cyclic olefin copolymer, optical materials) (See Reviews for cyclic olefin copolymers (See Reviews for cyclic olefin copolymers [4–9], syndiotactic polystyrene (thermal, chemical resistance) [10] and others. Since new polymers would be mostly prepared by incorporation of new comonomers (sterically encumbered, called *traditionally unreactive monomers* in

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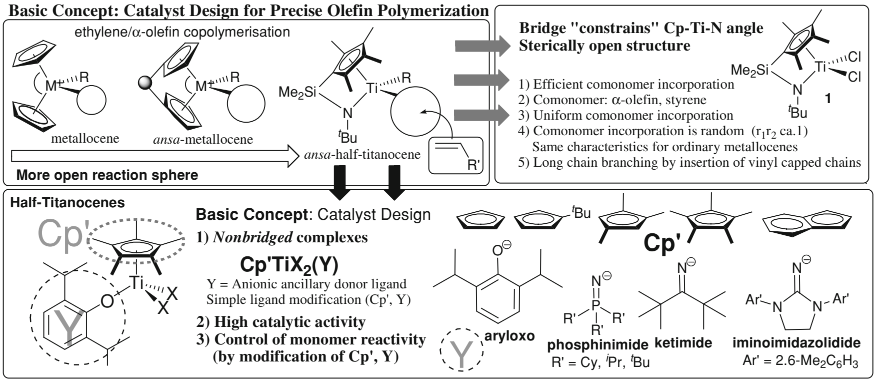
transition metal catalyzed coordination polymerization) in the copolymerization, it has thus been considered that design of the efficient transition metal complex catalysts that precisely control olefin polymerization should be the key for the success; the new catalysts described herein offer promising possibilities (See Reviews for cyclic olefin copolymers [4–9], See Reviews for metallocenes [11–14], See Reviews for linked half-titanocenes [15–17], See Reviews for non-bridged half-titanocenes [18–20], See Reviews for post-metallocenes [18–24], See Selected reviews for (co)polymerization of polar monomers [25–27], See Selected reviews for living polymerization [28–42]).

It has been recognized that the catalysts exhibiting remarkable activities with better comonomer incorporations should be desired for the successful design of an efficient transition metal catalyst for ethylene (co)polymerizations. It has been reported that bridged (*ansa*) metallocene-type complexes generally show better comonomer incorporation than the nonbridged (unbridged) analogues in ethylene/α-olefin copolymerization (See Reviews for metallocenes [11–14], Examples for ethylene/α-olefin copolymerizations using metallocenes and constrained geometry type catalysts [43–45]). The fact has been explained as that the bridged metallocenes possess rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky α-olefins (Scheme 2.1) (See Reviews for metallocenes [11–14]). Linked half-titanocenes containing amide ligand, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**) so called "constrained geometry catalyst (CGC)", have also been known to exhibit efficient comonomer incorporation (Scheme 2.1) [46–57], and the efficiency in α-olefin in ethylene/α-olefin copolymerization, that can be evaluated by using r_E values under the similar conditions, increases in the order: $Cp_2ZrCl_2 <$ *rac*-$Me_2Si[benz(e)Ind]_2ZrCl_2 < [Me_2Si(C_5Me_4)(N^tBu)]Ti–Cl_2$ (**1**) (Examples for ethylene/α-olefin copolymerizations using metallocenes and constrained geometry type catalysts [43–45]). This complex (CGC) was designed according to the analogous scandium complex [58, 59] and the reason for better comonomer incorporation has been explained as that *the bridge constrain more open Cp–Ti–N bond angle* offering better comonomer incorporation by allowing improved accessibility for (rather) bulky α-olefins (See Reviews for metallocenes [11–14], See Reviews for linked half-titanocenes [15–17]). Many researchers thus focused on designing the catalysts with "constrained geometry type" for the above reason (See Reviews for linked half-titanocenes [15–17, 46]).

2.2 Modified Half-Titanocenes as Olefin Polymerization Catalysts

Nonbridged half-titanocenes of the type, $Cp'TiX_2(Y)$ (Cp' = cyclopentadienyl group; Y = anionic donor ligand such as aryloxo [60–66], ketimide [67–74], phosphinimide [75–77], iminoimidazolidide (Copolymerization with α-olefin containing bulky substituents [78–80]) etc.; X = halogen, alkyl), as shown in



Scheme 2.1 Basic proposed concept for the catalyst design for half-titanocenes [11–20]

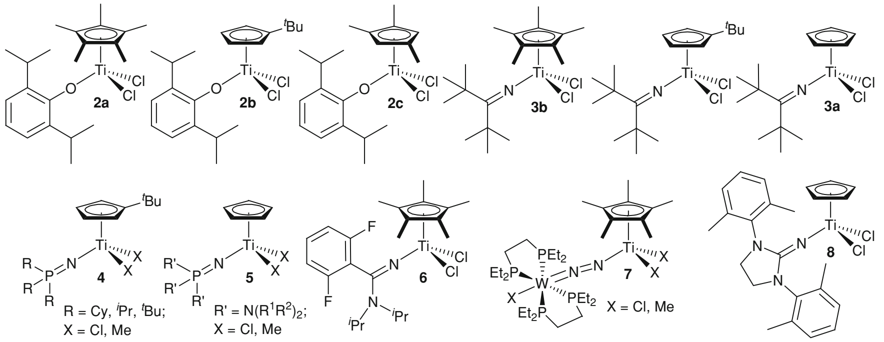
Scheme 2.2, have been considered as promising candidates for the efficient catalysts (Reviews for cyclic olefin copolymers [9], See Reviews for nonbridged half-titanocenes [18–20, 40–42], Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization, for example [60–77, 81]), because these complex catalysts display unique characteristics especially for synthesis of new polymers (See Reviews for nonbridged half-titanocenes [19, 20], Ethylene copolymerization with 2-methyl-1-pentene (disubstited α-olefin) [82, 83], Copolymerization with α-olefin containing bulky substituents [78–80], Copolymerization with norbornene [84–87], Copolymerization with cyclohexene, cyclopentene [88, 89], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90–95]) that cannot be prepared (or are very difficult to be prepared) by ordinary catalysts such as Ziegler-Natta, metallocenes [11–14], ‘constrained geometry’ type catalysts (CGC) (See Reviews for linked half-titanocenes [15–17]. We reported in 1998 that half-titanocenes containing an aryloxo ligand of the type, Cp’TiCl$_2$(OAr) (Cp’ = cyclopentadienyl group; OAr = aryloxo group, O-2,6-^{i}Pr$_2$C$_6$H$_3$ etc.), exhibited not only notable catalytic activities for olefin polymerization, but also for efficient 1-butene incorporation in the ethylene/1-butene copolymerization ([69], First patent application for Cp’-aryloxo complexes [96]; Related publications for synthesis and reactivity of cationic half-titanocene alkyl complexes containing aryloxo ligand [97–99]; See Related study (by the other group) concerning structure and activity correlation, effect of ion pairing and sterics on chain propagation for olefin polymerization by half-titanocenes containing aryloxides [100–102]). Therefore, there have been many examples concerning syntheses of complexes of this type and their use as olefin polymerization catalysts [19, 20], especially for ethylene polymerization. The selected examples in Cp’TiX$_2$(Y) that are known to be promising candidates as the efficient catalysts are shown in Scheme 2.2 (See Reviews for nonbridged half-titanocenes [18–20]; Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization [60–66]), [67–77, 81, 103–108].

2.2.1 Olefin Polymerization by Half-Titanocenes Containing Aryloxo Ligands

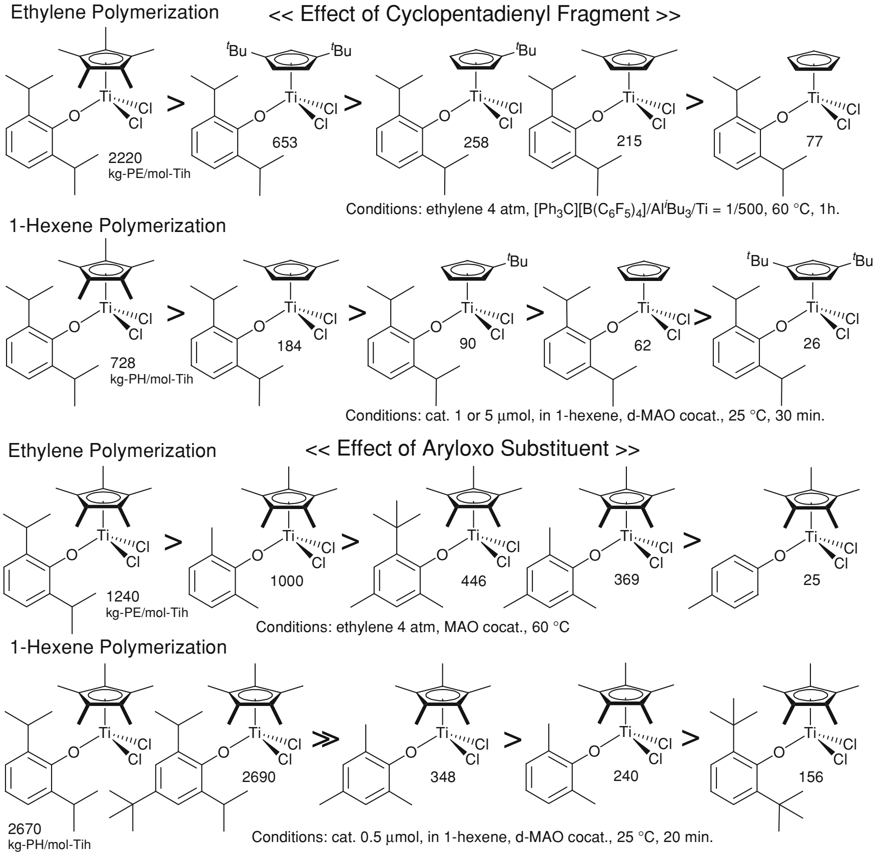
It has been known that the ligand modification is potentially important in order for metal catalyzed olefin polymerization to proceed with remarkable activities. For example, as shown in Scheme 2.3, substituents on both cyclopentadienyl and aryloxo ligands affect the activity for ethylene polymerization (Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization, for example [60, 61]).

$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2a**) exhibited notable activities, and the activity by $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ increased in the order: Cp'=Cp* ≫ $1,3\text{-}^tBu_2C_5H_3$ > $1,3\text{-}Me_2C_5H_3$, $^tBuC_5H_4$ ≫ Cp. The similar trend was observed in the syndiospecific styrene polymerization using a series of $Cp'Ti(OMe)_3$ complexes [40, 109, 110], and the fact would be assumed as due to a stabilization of the active site by more electron-donating substituents leading for the high activity. The $^tBu_2C_5H_3$ analogue showed lower catalytic activity in 1-hexene and 1-octene polymerization due to the steric bulk on Cp' (See Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization, for example [62, 64]). Steric bulk of the phenoxy ligand having substituents in the 2,6-position is important for exhibiting the high activity [1, 2]: this would play a role to stabilize the active species under the polymerization conditions in the presence of cocatalyst as well as to protect the probable side reaction with Al alkyls leading dissociation of the aryloxide (deactivation).

In order to explore the reason why both the Cp* and 2,6-diisopropylphenoxy ligand in **2a** are prerequisite for the remarkable activity in the ethylene polymerization, structures of various Cp and aryloxide analogues were determined by X-ray crystallography [60, 61]. On the basis of structural data in $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, the bond angle (173.0°) of Ti–O–C (phenoxy) for $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2a**), which was the most effective catalyst precursor, is significantly different from those for the other Cp derivatives, (Cp'=Cp, $1,3\text{-}^tBu_2C_5H_3$, 163.0–163.1°): the large Ti–O–C bond angle would lead to more O → Ti π donation into Ti (Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization, for example [60, 61]). However, the bond angle for the di-*tert*-butyl analogue, $Cp^*TiCl_2(O\text{-}2,6\text{-}^tBu_2C_6H_3)$, is small (155.5°): the bond angles of Ti–O–C (phenyl) the diisopropyl analogues, (173.0, 174.6° for Ar=$2,6\text{-}^iPr_2C_6H_3$, $2,6\text{-}^iPr_2\text{-}4\text{-}^tBuC_6H_2$, respectively) [60, 61, 111] are larger than those in the other Cp* derivatives (155.5–162.3°: Ar=$2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, $2,6\text{-}^tBu_2C_6H_3$, $2,6\text{-}Ph_2C_6H_3$ etc.) except $Cp^*TiCl_2(O\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}^tBu_2C_6H)$ (176.9°) [97–99, 111]. Moreover, $Cp^*Ti(X^1)(X^2)(O\text{-}2,6\text{-}^iPr_2\text{-}4\text{-}R'C_6H_2)$ (X^1, X^2=Cl, Cl, Me, Me, Me, CF_3SO_3, R'=H or ^tBu) possessed relatively large bond angles in all cases (166.2–174.6°). These results thus clearly suggest that the unique Ti–O–C (phenyl) bond angle, leading to stabilize the catalytically-active species by more O → Ti π donation into the titanium, are dependent upon the substituents in both cyclopentadienyl and aryloxo ligands.



Scheme 2.2 Selected modified *nonbridged* half-titanocenes exemplified in this article as effective catalyst precursors



Scheme 2.3 Effect of cyclopentadienyl fragment (Cp') and aryloxo substituents toward the activity in olefin polymerization by Cp'$TiCl_2$ cocatalyst system

Simple calculations by geometry optimizations of the proposed catalytically active species, [Cp'Ti(pentyl)(OAr)(ethylene)]$^+$ (Fig. 2.1) with a series of cyclopentadienyl and aryloxo ligands, suggest that an introduction of methyl group (or *tert*-butyl group) onto Cp' leads to stabilization of the catalytically-active species ($C_5Me_5 > Me_3C_5H_2 > Me_2C_5H_2 > C_5H_5$) [109, 110]. The aryloxo substituent in the *ortho* position not only affects the stabilization, but also affects the R–Ti–ethylene bond angle that should be important for the subsequent insertion. It was thus revealed that the cationic species containing Cp* and diisopropylphenoxy ligands showed both better stabilization and possessed geometry for the subsequent insertion (narrow bond angle). Although the results are on the basis of simple PM3 semiempirical level, this would be considered as the origin why **2a** showed the high activity affording the polymer with unimodal distributions in this catalysis.

The observed activity was extremely low when 1-hexene polymerization was conducted in the presence of $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ and $B(C_6F_5)_3\text{-}Al^iBu_3$, whereas the polymerization took place in a quasi-living manner with significant activity at −30 °C when $[Ph_3C][B(C_6F_5)_4]$ was used in place of $B(C_6F_5)_3$ [112]. The reaction with $B(C_6F_5)_3$ in toluene-d_8 afforded decomposed compound, $Cp^*Ti(C_6F_5)[CH_2B(C_6F_5)_2](O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$, (and/or intermediates) even at −70 °C, whereas no decomposition was observed if the reaction was employed with $[Ph_3C][B(C_6F_5)_4]$ [113]. The species generated from the reaction consumed 1-hexene exclusively even at −30 °C, suggesting that the generated cationic Ti(IV) species play a role in this catalysis.

Rothwell et al. also prepared a $CpTiMe_2(OAr)$ complex containing an *ortho*-naphthylphenoxide ligand [97–99], and addition of $B(C_6F_5)_3$ in benzene gave thermally unstable cationic complex, $CpTiMe[(\mu\text{-}Me)B(C_6F_5)_3](OAr)$, which then gradually decomposed at ambient temperature to afford the neutral species, $CpTi(C_6F_5)[CH_2B(C_6F_5)_2](OAr)$, followed by methane elimination (Scheme 2.4) [97–99].

2.2.2 Selected Examples in Olefin Polymerization by Half-Titanocenes Containing the Other Anionic Ancillary Donor Ligands

Ligand effect toward the activity in ethylene polymerization using a series of half-titanocenes containing phosphinimide ligand of type, $Cp'Ti(N{=}PR_3)X_2$ (**4**, Table 2.1), were explored (Scheme 2.5) [75–77], because a sterically bulky $N{=}PR_3$ ligand as the steric equivalent to cyclopentadienyl group (Cp') [75–77] would provide the similar sterically/electronically environment to Cp' [114, 115]. These complexes exhibited remarkable activities in the presence of MAO, and the activity improved with the combination of $[Ph_3C][B(C_6F_5)_4]$: substituents on both Cp' and $N{=}PR_3$ ligands play a role for exhibiting the high activity, and use of $N{=}PCy_3$ ligand was

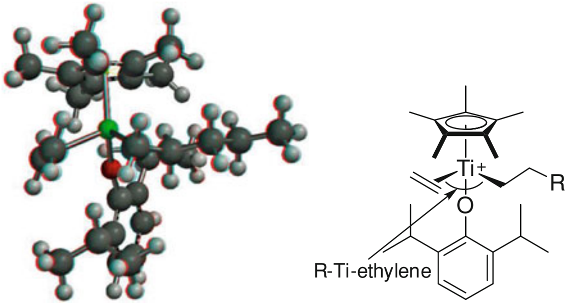
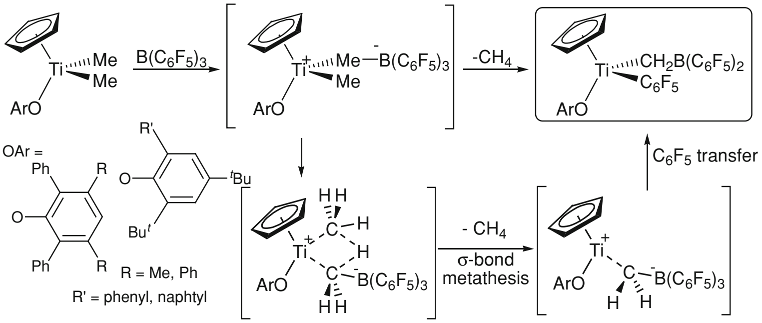


Fig. 2.1 Assumed catalytically-active species, the optimised structure [234]



Scheme 2.4 Deactivation pathway by reacting with $B(C_6F_5)_3$ [97–99]

Table 2.1 Ethylene polymerization by Cp'$TiX_2(N{=}PR_3)$ [**4**, Cp'=Cp, *tert*-BuC_5H_4 (^{t}BuCp); X=Cl, Me; R=Cy, ^{i}Pr, ^{t}Bu]—cocatalyst systems[a]

Complex	Cocatalyst	Activity[b]	$M_w^c \times 10^{-4}$	M_w/M_n^c
$CpTiCl_2(N{=}P^tBu_3)$	MAO	500	8.99	2.4
$CpTiMe_2(N{=}P^tBu_3)$	$Ph_3CB(C_6F_5)_4$	401	16.6	3.4
$^tBuCpTiCl_2(N{=}P^tBu_3)$	MAO	881	6.54	2.4
$^tBuCpTiMe_2(N{=}PCy_3)$	$Ph_3CB(C_6F_5)_4$	1807	31	7.5
$^tBuCpTiMe_2(N{=}P^iPr_3)$	$Ph_3CB(C_6F_5)_4$	1193	25.9	9.9
$^tBuCpTiMe_2(N{=}P^tBu_3)$	$Ph_3CB(C_6F_5)_4$	1296	32.1	12.3
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$	MAO	630		

[a] Cited from Ref. [75], *Conditions* catalyst 0.01–0.03 mmol, toluene, ethylene 1 atm, 25 °C, 0.5–3 min, MAO (Al/Ti = 500, molar ratio) or $Ph_3CB(C_6F_5)_4$ (B/Ti = 2)

[b] Activity in kg-polymer/mol-Ti·h

[c] GPC data in *o*-dichlorobenzene versus polyethylene standards

effective. The $^tBuC_5H_4$ analogues were more suited than the Cp analogues, suggesting that electron-donating substituents on Cp' increase the activity. Analogous zirconium complexes showed low activities for ethylene polymerization [116, 117]. The tris(amido)phosphinimide analogues, Cp'$TiX_2[N{=}P(NR_2)_3]$ (**5**, X=Cl, Me), showed

Table 2.2 Ethylene polymerization by $Cp'TiX_2[NP(NR^1R^2)_3]$ (**5**)—cocatalyst systems[a]

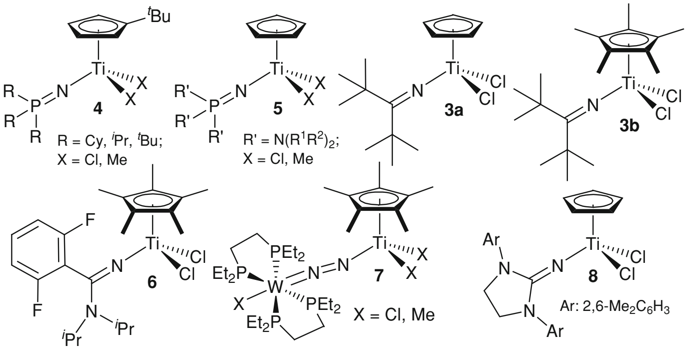
Complex (μmolL^{-1})	Cocat.	Time /min	Activity[b]	$M_n^c \times 10^{-4}$	M_w/M_n^c
$Cp^*TiCl_2[N{=}P\{N(Et)Ph\}_3]$ (50)	MAO	30	200	12.61	4.02
$CpTiMe_2[N{=}P\{N(Et)Ph\}_3]$ (4)	Al/B[d]	10	4200	43.25	1.92
$Cp^*TiMe_2[N{=}P(NMe_2)_3]$ (4)	Al/B[d]	10	4200	14.08	4.92
$Cp^*TiMe_2[N{=}P(NEt_2)_3]$ (4)	Al/B[d]	10	4700		
$Cp^*TiMe_2[N{=}P(NPr_2)_3]$ (4)	Al/B[d]	10	10000		
$Cp^*TiMe_2[N{=}P\{N(Et)Ph\}_3]$ (4)	Al/B[d]	10	4200	32.46	2.03
$Cp^*TiMe_2[N{=}P^iPr_3]$ (4)	Al/B[d]	10	5200	49.34	2.05
$CpTiMe_2[N{=}P^tBu_3]$ (4)	Al/B[d]	10	5600	43.78	1.80
Cp_2ZrMe_2 (4)	Al/B[d]	10	16000	17.5	1.89

[a] Cited from Ref. [103], *Conditions* ethylene 2 atm, 30 °C, toluene 600 mL, 1000 rpm, 500 equiv of MAO or Al/B

[b] Activity in kg/mol-Ti·h·atm

[c] GPC data in *o*-dichlorobenzene versus polyethylene standards

[d] Al/B=$Al^i Bu_3/B(C_6F_5)_3$, 2 equiv of $B(C_6F_5)_3$; 20 equiv of $Al^i Bu_3$



Scheme 2.5 Selected modified *nonbridged* half-titanocenes exemplified in this section

high activities in the presence of $B(C_6F_5)_3$ (Table 2.2) [103], and the activity increased upon increasing the steric bulk.

In contrast, no significant differences in the activities were observed in ethylene polymerization using $Cp'TiCl_2(N{=}C^tBu_2)$ (Cp'=Cp, $^tBuC_5H_4$, Cp*) [70], whereas the activities in 1-hexene polymerizations were affected by the Cp' employed (Table 2.3) [70, 71]. 1-Hexene polymerization by $CpTiCl_2(N{=}C^tBu_2)$ took place efficiently, and a first order relationship between the monomer concentration and the reaction rate was observed, strongly suggesting that the apparent decrease is due to the decrease in the 1-hexene concentration not due to a deactivation of the catalytically-active species. The activities by $Cp'TiCl_2[N{=}C(R^1)R^2]$ were strongly affected by the ketimide substituents [69, 87], and the complexes containing two ^{t}Bu groups as the ketimide substituents were effective to give polymers with unimodal molecular weight distributions, in other words, to proceed with uniform catalytically-active species.

Table 2.3 Ligand effect in ethylene polymerization by Cp'TiCl$_2$(N=C^{t}Bu$_2$) (Cp'=Cp, ^{t}BuC$_5$H$_4$, Cp*, indenyl)—MAO catalyst systems[a]

Cp' (μmol)	Olefin	Activity[b]	$M_w^c \times 10^{-5}$	M_w/M_n^c
Cp (0.2)	Ethylene	13400	9.66	1.9
^{t}BuC$_5$H$_4$ (0.2)	Ethylene	14300	9.9	2.1
Cp* (0.2)	Ethylene	16600	10.4	2.2
Indenyl (0.2)	Ethylene	7700	5.61	2.1
Cp (0.25)	1-hexene	16800	6.17	1.6
^{t}BuC$_5$H$_4$ (2.5)	1-hexene	1310	2.85	1.7
Cp* (2.5)	1-hexene	569	1.30	1.6
Indenyl (0.25)	1-hexene	11900	2.81	1.7

[a] Cited from Refs. [70, 71], *Conditions* (ethylene) complex 0.2 μmol, toluene 40 mL, ethylene 4 atm, MAO white solid 3.0 mmol (Al), 40 °C, 10 min; *Conditions* complex in toluene 0.5 mL, 1-hexene 10 mL, 25 °C, 20 min, MAO white solid 2.0 mmol

[b] Activity in kg-polymer/mol-Ti·h

[c] GPC data in *o*-dichlorobenzene or THF versus polystyrene standards

Cp*TiX$_2$[N=C(2,6-R$^1_2$C$_6$H$_3$)(NR$^2_2$)] [**6**, Scheme 2.2, R^1=F, Cl; R^2=^{i}Pr, Cy etc.; X=Cl, Me] exhibited remarkable activities for ethylene/propylene copolymerization (for synthesis of EPDM, ethylene–propylene–diene copolymer) [104, 105], and the activity was highly affected by the substituents (R^1,R^2); Cp*TiX$_2$[N(2,6-F$_2$C$_6$H$_3$)(N^{i}Pr$_2$)] exhibited notable activity [104]. Ethylene polymerization and copolymerization of ethylene with 1-hexene catalyzed by heterobimetallic dinitrogen complex (**7**, Scheme 2.5) were reported [106]. The complex exhibited high activities, but the 1-hexene incorporation was not sufficient probably due to bulky substituent in the anionic donor ligand.

Half-titanocenes containing iminoimidazolidide ligand, CpTi(CH$_2$Ph)$_2$[1,3-(2,6-Me$_2$C$_6$H$_3$)$_2$-(CH$_2$N)$_2$C=N] (**8**, Scheme 2.5) exhibited notable activities for ethylene polymerization in the presence of B(C$_6$F$_5$)$_3$ cocatalyst [81]. The catalyst was reported to show higher activities than the CpTi(CH$_2$Ph)$_2$(NP^{t}Bu$_3$) under the same conditions (in the presence of partially hydrolyzed Al^{i}Bu$_3$, TIBAO). However, comonomer incorporations in the copolymerization of ethylene with α-olefin, styrene, norbornene were not as high as those by the aryloxo [60–66, 90–95] or ketimide analogues [84–87]. Taking into account the facts described above, the role of anionic donor ligand should be the key for design of more effective catalyst precursors in this catalysis.

2.2.3 *Copolymerizations of Ethylene with Sterically Encumbered α-olefins*

2.2.3.1 Copolymerizations of Ethylene with Linear α-olefins

Table 2.4 summarizes selected results in copolymerizations of ethylene with α-olefins using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2a**), CpTiCl$_2$(N=C^{t}Bu$_2$) (**3a**), and the

Table 2.4 Selected results in ethylene copolymerization with 1-hexene, 1-dodecene by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2a**), $CpTiCl_2(N{=}C^tBu_2)$ (**3a**), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**)-MAO catalyst systems[a]

Complex (μmol)	Comonomer[b] (M)	Ethylene /atm	Temp/°C	Activity[c]	$M_n^d \times 10^{-5}$	M_w/M_n^d	Cont.[e] /mol%
$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2a**) (0.08)	1-hexene (0.73)	7	40	103000	2.30	1.98	24.6
$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2a**) (0.07)	1-hexene (1.45)	7	40	263000	1.80	1.87	38.1
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**) (0.60)	1-hexene (0.73)	7	40	14600	5.17	2.30	23.7
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**) (0.65)	1-hexene (1.45)	7	40	6960	3.98	2.21	39.4
$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2a**) (0.01)	1-dodecene (0.75)	6	25	230000	1.87	1.99	19.2
$CpTiCl_2(N{=}C^tBu_2)$ (**3a**) (0.01)	1-dodecene (0.75)	6	25	123000	4.84	1.97	15.5
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**) (0.10)	1-dodecene (0.75)	6	25	24800	3.91	2.09	19.2

[a] Cited from Refs. (Our initial efforts in olefin polymerization and ethylene/α-olefin copolymerization, for example, [60–66]), *Conditions* toluene and comonomer total 30 mL, dried MAO (prepared by removing toluene and $AlMe_3$ from the ordinary MAO) 3.0 (or 2.0) mmol, 25 °C, 10 min

[b] Initial comonomer concentration in mmol/mL

[c] Activity in kg-polymer/mol-Ti·h

[d] GPC data in *o*-dichlorobenzene versus polystyrene standards

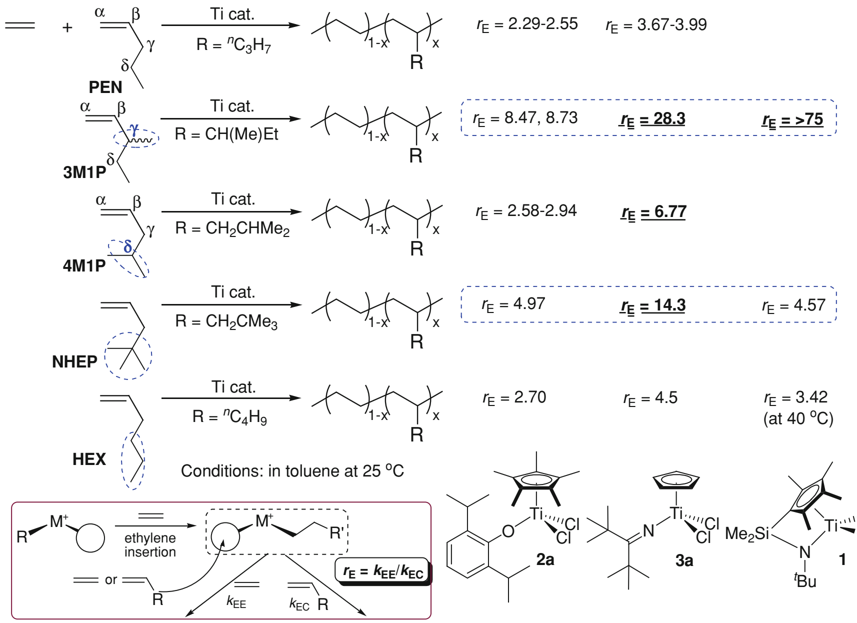
[e] Comonomer contents estimated by ^{13}C NMR spectra

[f] Cited from Ref. [61], polymerization for 6 (or 4) min

constrained geometry catalyst (CGC), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**), in the presence of MAO cocatalyst [63, 64, 71, 80]. The Cp*-aryloxo analogue (**2a**) exhibited remarkable activities for copolymerization of ethylene with 1-butene [61], 1-hexene [63, 64], and 1-decene [80] affording high molecular weight copolymers with uniform compositions. The observed activities (calculated from the polymer yields) by **2a** were higher than those by **1**, and the 1-hexene contents in the resultant copolymers by **2a** were close to those by **1** under the same conditions [63, 64]. The activity by 2a increased upon increasing the 1-hexene concentration, whereas the activity by CGC (**1**) decreased upon increasing 1-hexene concentration [64]. The $^tBuC_5H_4$ analogue, $(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2b**), showed better 1-hexene incorporation than **2a**, whereas the $^tBu_2C_5H_3$ analogue showed the less efficient incorporation.

The Cp-ketimide analogue (**3a**) also exhibited high activities in the copolymerizations [71], but the comonomer incorporations were less efficient than those by **2a** and **1**, suggesting that the comonomer incorporation was affected by the anionic donor ligand. The activities by the Cp*-ketimide analogue, $Cp^*TiCl_2(N{=}C^tBu_2)$ (**3b**), exhibited better catalyst performance than **3a** under high temperature (160 °C) and high pressure (1500 psi, 102 atm), continuous solution polymerization conditions [69].

Effect of the centered metal toward the activity and the comonomer incorporation were explored in ethylene (co)polymerization using a series of $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ (M=Ti, Zr, Hf; R=Ph, ^tBu) in the presence of MAO cocatalyst [118]. The activity in ethylene polymerization was affected by the centered metal employed [Ti > Zr > Hf]; the phenyl analogues (R=Ph) showed higher activities than the *tert*-butyl analogues (R=^tBu). The ethylene/1-octene copolymerizations afforded copolymers with uniform molecular weight distributions, except $Cp^*TiCl_2(O\text{-}2,6\text{-}^tBu_2C_6H_3)$, where both the activity and the 1-octene incorporation were highly affected greatly by the centered metal employed: $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2a**) was the most suitable in terms of both activity and the 1-octene incorporation. The attempted copolymerization of ethylene with 2-methyl-1-pentene (2M1P) using the above complexes—MAO catalysts afforded linear polyethylene, whereas **2a** incorporated 2M1P under the same conditions [118]. The copolymerizations by $(1,3\text{-}Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, $CpTiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, $Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ and $(1,3\text{-}^tBu_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ afforded polymers with bimodal molecular weight distributions, whereas the resultant copolymers possessed uniform molecular weight distributions in the copolymerizations by the Cp*-aryloxo analogue (**2a**), $^tBuC_5H_4$ analogue (**2b**), and $^tBu_2C_5H_3$ analogue [64]. Therefore, effect of ligand substituents plays an essential role in the ethylene copolymerization by $Cp'TiCl_2(OAr)$–MAO catalyst systems not only exhibiting high catalytic activity, but also affording high molecular weight copolymer with uniform distribution [64].



Scheme 2.6 Copolymerization parameters (*r* values) in ethylene copolymerizations using half-titanocenes [80]

2.2.3.2 Copolymerizations of Various Substituted Pentenes

Effect of structure/ligand toward both the catalytic activities and the monomer reactivities in the ethylene copolymerizations with various pentenes [1-pentene, 4-methyl-1-pentene (4M1P), 3-methyl-1-pentene (3M1P, mixture of *R* and *S*), 4,4-dimethyl-1-pentene (NHEP)] using the Cp*-aryloxo analogue (**2a**), the Cp-ketimide analogue (**3a**), the constrained geometry catalyst (1) were conducted in the presence of MAO. Scheme 2.6 summarizes r_E, r_C (E = ethylene, C = comonomer) and $r_E \cdot r_C$ values for the copolymerizations by the Cp*-aryloxo analogue (**2a**), the Cp-ketimide analogue (**3a**) and CGC (**1**) based on experimental results (in toluene at 25 °C).

The Cp*-aryloxo analogue (**2a**) exhibited both remarkable catalytic activity and efficient 3M1P incorporation in the ethylene/3M1P copolymerization; the r_E value (8.73) was much smaller than those by **1** (92), **3a** (28.3). Both **2a** and **1** showed better NHEP incorporation than **3a** in the ethylene/NHEP copolymerization; the rather large r_E value by **3a** (6.77) compared to those by 2a (2.58–2.94) was also obtained in the copolymerization with 4M1P [80]. The results suggest that the monomer reactivity by **3a** was influenced by the substituent in the δ-position (in addition to the substituent in the γ-position), whereas the monomer reactivity by **1** was more influenced by the substituent in the γ-position (Scheme 2.6). The monomer reactivities (r_E values) are thus strongly influenced not only by both the substituent in the olefins and the (electronic and steric) nature of the catalytically active species (structure, ligand set employed). The $r_E \cdot r_C$ values by **2a** were small in all cases, suggesting that the comonomer incorporations were rather alternating, whereas the copolymerization by **1** proceeded in a random manner (comonomer incorporations were random, $r_E \cdot r_C$=ca. **1**) except the copolymerization with 3M1P. The observed differences emphasize unique characteristics for using this half-titanocenes for precise olefin copolymerization [19, 63, 64, 71, 80].

2.2.3.3 Copolymerizations of Ethylene with 2-methyl-1-Pentene

Synthesis of ethylene copolymers containing 2,2-disubstituted-1-olefins is one of the promising targets, because only a few examples were known in the metal catalyzed olefin polymerization [119]. For example, ethylene/isobutene (IB) copolymerization using $[(CH_2CH_2)(indenyl)_2]ZrCl_2$—MAO catalyst system afforded a copolymer with low IB content (<2.8 mol%) even under large IB stoichiometric excess conditions (IB:ethylene = 4000:1) [120]. The resultant copolymer in the ethylene/2-methyl-1-pentene (2M1P) copolymerization by $[Me_2Si(MeC_5H_3)(N\text{-cyclododecyl})]TiMe_2$—$[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst system, possessed low molecular weight with broad molecular weight distributions ($M_n = 10780$, $M_w/M_n = 5.9$, 2M1P content 9.0 mol%) [121], although the ethylene/IB copolymerization (MAO cocatalyst) afforded a copolymer with 45 mol% IB content under certain conditions (ethylene 0.34 bar, $M_n = 13200$, $M_w/M_n = 2.5$) [121].

Notable improvement in the IB incorporation (30 times increase in the IB/ethylene reactivity ratio) had recently been achieved by using a binuclear constrained geometry type half-titanocene in the presence of a bifunctional borate cocatalyst (Scheme 2.7) [122, 123], and it was proposed that the increased selectivity for highly encumbered comonomer enchainment, presumably facilitated via cooperative comonomer capture/binding/delivery by the proximate cationic centers ([122], Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [123, 124]. However, both the activity and the IB incorporation were sensitive to the cocatalyst and the activity was slightly decreased upon increasing the catalyst/cocatalyst nuclearity (Table 2.5).

Copolymerization of ethylene with 2M1P using the Cp*-aryloxo analogue (**2a**)—MAO catalyst system took place with rather efficient 2M1P incorporation (Table 2.6), whereas the 2M1P incorporations by Cp_2ZrCl_2, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**), $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp'=Cp (**3a**), Cp* (**3b**)]—MAO catalyst systems were negligible under the same conditions. Effect of ligand substituents toward the catalytic activities and the 2M1P incorporations were also explored, and use of both Cp* and 2,6-diisopropylphenoxy ligands were found to be important to obtain a copolymer with a rather efficient and uniform 2M1P incorporation as well as with moderate catalytic activities. No distinct differences in 2M1P incorporations were seen in the copolymerization by **2a** in the presence of various cocatalysts [methylaluminoxane (MAO), methyl-isobutyl-aluminoxanes (modified MAO,

Scheme 2.7 Typical dinuclear catalyst/cocatalyst systems in ethylene copolymerizations [122, 123]

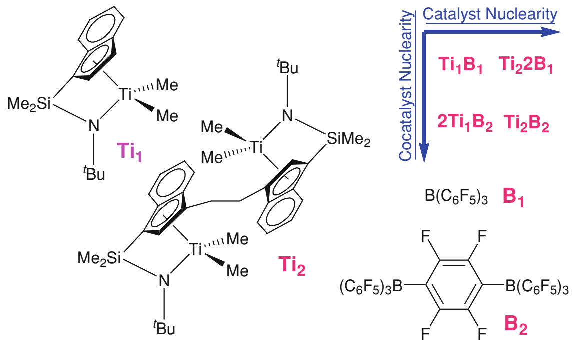


Table 2.5 Copolymerization of ethylene with isobutene (IB) catalyzed by binuclear (co)catalysts[a]

Cat. (μmol)	Cocat.	Time /min	Activity[b]	$M_w^c \times 10^{-5}$	M_w/M_n^c	Cont.[d] /mol%
Ti₁ (10)	**B₁**	5	960	5.77	2.13	3.1
Ti₁ (10)	**B₂**	5	440	3.05	2.16	9.5
Ti₂ (5)	**B₁**	10	360	4.90	2.41	7.3
Ti₂ (5)	**B₂**	10	280	1.68	3.67	15.2
Ti₁ (10)	**MAO**[e]	60	39	4.87	2.52	2.9
Ti₂ (5)	**MAO**[e]	240	11	3.55	2.87	6.2

[a] Cited from Refs. [122, 123], *Conditions* Polymerizations carried out on a high-vacuum line at 24 °C in 100 mL of toluene under 1.0 atm ethylene pressure, isobutene 1.2 mmol/mL (M)

[b] Activity in kg-polymer/mol-Ti

[c] GPC data in *o*-dichlorobenzene versus polystyrene standards

[d] Estimated from ^{13} C NMR spectra

[e] Al:Ti = 1000:1

Table 2.6 Copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by Cp'TiCl$_2$(Y) [Y=O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp'=Cp* (**2a**) ^{t}BuC$_5$H$_4$ (**2b**); Y=N=C^{t}Bu$_2$, Cp'=Cp (**3a**), Cp* (**3b**)], [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**1**), Cp$_2$ZrCl$_2$–MAO catalyst systems[a]

Cat. (μmol)	Ethylene /atm	Activity[b]	$M_n^c \times 10^{-4}$	M_w/M_n^c	2M1P[d] /mol%
2a (0.5)	6	5760	10	1.8	5.7
2a (0.5)	4	2680	4.9	1.6	9.4
2b (2.0)	4	324	1.8	2.3	5.1
3a (0.2)	6	6960	34	1.8	0.3
3b (0.2)	6	7770	63	1.9	0.3
1 (1.0)	6	1840	12	2.4	0.3
Cp$_2$ZrCl$_2$(0.2)	6	4590	148	2.7	trace

[a] Cited from Ref. [70], *Conditions* 2M1P 2.70 mmol/mL, 2M1P + toluene total 30 mL, d-MAO 3.0 or 4.5 mmol, 25 °C, 6 or 10 min

[b] Activity in kg-polymer/mol-M·h (M=Ti, Zr)

[c] GPC data in *o*-dichlorobenzene versus polystyrene standards

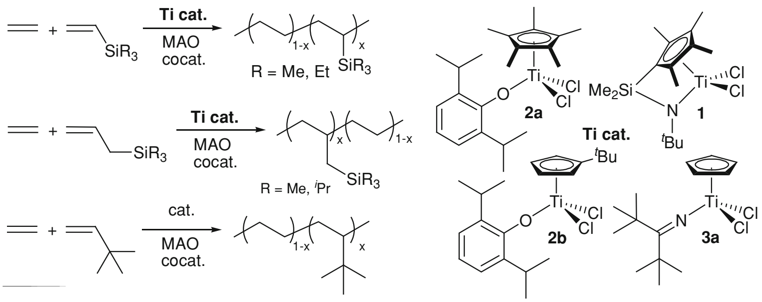
[d] 2M1P in copolymer (mol%) estimated by ^{13} C NMR spectra

MMAOs), borates], and the nature of the ligands thus predominantly affects the 2M1P incorporation. The 2M1P contents in the copolymers prepared by the $^tBuC_5H_4$-aryloxo analogue (**2b**) were lower than those by **2a** under the same conditions, whereas **2b** exhibited better 1-hexene incorporation than **2a** in the ethylene/1-hexene copolymerization [63, 64]. On the basis of the calculation of the optimised geometries for assumed catalytically-active [cationic Ti(IV) alkyl] species after 2M1P insertion [93, 94], this may be explained as due to the steric hindrance of *tert*-butyl group on Cp' against the methyl group in Cp* (difference in the stabilization of ethylene coordination after insertion of 2M1P) [125].

2.2.3.4 Copolymerization of *Tert*-butylethylene, α-olefins Containing Trialkylsilyl Group

Precise, efficient functionalization of polyolefins under mild conditions is considered as an attractive subject, and the controlled incorporation of the desired functionalities by the direct copolymerization has been one of the most promising approaches (See Selected reviews for (co)polymerization of polar monomers (Selected reviews for (co)polymerization of polar monomers: [25, 32], See Book and reviews [126–129], See Recent examples for transition metal catalyzed coordination copolymerization with monomers containing polar functionalities [130–137], Examples for late transition metal catalysts [138–141], Selected examples (ATRP, Nitroxide, RAFT etc.) [142–152]). However, the introduction in the copolymerization of ethylene or propylene with (protected) polar monomer(s) faces difficulties due to catalyst poisoning as well as to the interaction of the centered metal with the functional groups. The copolymerizations of ethylene with certain alkenylsilanes [$CH_2{=}CH(CH_2)_nSiH_3$], n = 1, 2, 4, 6 etc.] using (dinuclear) linked half-titanocenes have been known as a promising route [153, 154], but the activity generally decreased upon increasing the comonomer content(s); the silane(s) also play a role as the chain transfer reagent(s) [154]. The copolymerization of ethylene with allyltrimethylsilane (ATMS) by certain metallocenes was also known (Chain transfer by Si [155–159]), but both the activities and the M_n values in the copolymers decreased depending on the ATMS contents. This is because ATMS also plays the role of chain transfer reagent due to a favored β-hydrogen elimination after bulky ATMS insertion (Previous reports for polymerization of ATMS by metallocenes [160, 161]).

The copolymerization with ATMS by $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2a**) proceeded efficiently, affording high molecular weight copolymers with uniform molecular weight distributions (Scheme 2.8, Table 2.7) [162, 163]. The activity by **2a** increased upon increasing the initial ATMS concentration and/or ethylene pressure. The Cp-ketimide analogue, $CpTiCl_2(N{=}C^tBu_2)$ (**3a**) showed less efficient ATMS incorporation in the copolymerization under the same conditions, but exhibited much higher catalytic activity than **2a**, affording high molecular weight copolymers with unimodal molecular weight distributions. The activity increased



Scheme 2.8 Copolymerizations of ethylene with vinyltrimethylsilane (VTMS), allyltrimethylsilane (ATMS), and with *tert*-butyl ethylene (TBE) [79, 162, 163]

Table 2.7 Copolymerization of ethylene with CH_2=$CHCH_2SiMe_3$ (ATMS), CH_2=$CHSiMe_3$ (VTMS), and with *tert*-butylethylene (TBE) using Cp’$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) [Cp’=Cp* (**2a**), $^tBuC_5H_4$ (**2b**)], $CpTiCl_2(N$=$C^tBu_2)$ (**3a**), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**), and Cp_2ZrCl_2—MAO catalyst systems[a]

Complex (μmol)	Comonomer (M)	Ethylene / atm	Activity[b]	$M_n^c \times 10^{-4}$	M_w/ M_n^c	Cont.[d] / mol%
2a (0.50)	ATMS (1.05)	6	3550	2.78	2.7	48.8
2a (0.50)	VTMS (1.15)	6	1870	30.5	1.9	5.1
2b (0.20)	VTMS (1.15)	6	92	1.41	2.8	13.6
3a (0.05)	ATMS (1.05)	6	47500	28.3	2.6	30.3
3a (1.00)	VTMS (1.15)	6	3730	57.3	2.3	11.9
1 (0.25)	VTMS (1.15)	6	2280	36.7	2.5	10.4
Cp_2ZrCl_2 (10.0)	VTMS (1.15)	6	23	0.56	3.9	trace
2a (0.20)	TBE (3.9)	2	2880	20.4	2.0	1.7
2b (1.00)	TBE (3.9)	2	1130	5.31	2.1	6.3
2b (1.00)	TBE (3.9)	4	2020	8.17	2.4	3.3
3a (0.40)	TBE (3.9)	2	1880	13.9	1.9	trace
1 (1.00)	TBE (3.9)	2	1190	11.9	2.1	none
Cp_2ZrCl_2 (0.05)	TBE (3.9)	2	24300	56.3	2.4	none

[a] Cited from Refs. [79, 162] and [163], *conditions* (AMTS, VMTS) comonomer 10 mL; comonomer + toluene total 30.0 mL, dried MAO 3.0 mmol, ethylene 6 atm, 25 °C; 10 min; *conditions* (TBE) ethylene 2 atm, TBE 5.0 mL, toluene 5.0 mL, dried MAO 5.0 mmol, 25 °C, 10 min

[b] Activity in kg-polymer/mol-M·h (M=Ti, Zr)

[c] GPC data in *o*-dichlorobenzene versus polystyrene standards

[d] Comonomer content estimated by ^{13} C NMR spectra

upon increasing the ATMS concentration and the ethylene pressure, and the M_n values in the copolymers were independent of the ATMS contents.

Vinyltrialkylsilanes should be considered as better comonomers in terms of the direct functional group introduction into the polyethylene (or polypropylene) backbone as well of their use as cross-linking reagents to improve thermal properties (See Preparation of poly(vinylsilane)s [164–166]). These sterically encumbered olefins are, however, very difficult to coordinate into the metal center in ordinary metallocenes (Equilibrium constants for alkene coordination to $(MeC_5H_4)_2Zr^+(O^tBu)(ClCD_2Cl)$ [167]), and no reports for the copolymerization had been published until recently (See For reported examples of insertion of vinyltrimethylsilane into cationic zirconium complexes [168–171]).

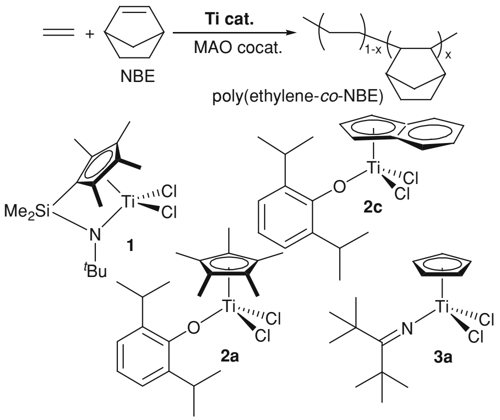
The Cp*-aryloxo analogue (**2a**) incorporated vinyltrimethylsilane (VTMS) into polyethylene with moderate catalytic activities (Scheme 2.8, Table 2.7), and the resultant copolymers possessed high molecular weights with uniform molecular weight distributions. The Cp-ketimide analogue (**3a**) exhibited both higher catalytic activities and better VTMS incorporations than **2a** [163]. Efficient synthesis of high molecular weight copolymers with uniform compositions could be achieved by adopting **3a**, although both the activity and the M_n values seemed to decrease upon the increasing VTMS contents. The copolymerization by the constrained geometry catalyst (**1**) also proceeded efficiently (Copolymerization with α-olefin containing bulky substituents [79]).

More recently, the *tert*-BuC_5H_4 analogue (**2b**) exhibited rather efficient TBE incorporation in the copolymerization, whereas the Cp'-ketimide analogue (**3a**, **b**), constrained geometry catalyst (**1**), Cp_2ZrCl_2 did not incorporate TBE under the same conditions (Scheme 2.8, Table 2.7) [79]. Effect of both the cyclopentadienyl fragment (Cp') and the anionic donor ligands (Y) in $Cp'TiX_2(Y)$ plays a crucial role for the successful copolymerization, as seen in the above copolymerization.

2.2.4 Copolymerization with Cyclic Olefins

Certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity-, and heat-resistance (high glass transition temperature, T_g).$^{2a-d}$ Three processes such as (1) ring-opening metathesis polymerization (ROMP) of multi-cyclic olefins and the subsequent hydrogenation, (2) coordination copolymerization of ethylene with cyclic olefins, (3) homopolymerization of cyclic olefins, are generally adopted for the practical production. In particular, the copolymerization route seems promising, because the desired properties can be tuned by their compositions (cyclic olefin contents etc.) as well as their microstructures (including tacticity).

Many examples were thus known for the copolymerization of ethylene with norbornene (NBE) using ordinary metallocenes [172–176], linked half-titanocenes (CGC) [56, 57, 120], half-titanocenes [84–87], and other so-called non-metallocenes [177–180]. However, successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (>50 mol%), which possess high T_g (>150 °C), were limited. This is not only because both the activity and the molecular weights in the copolymer decrease upon increasing NBE contents, but also because the microstructure in the copolymer possessed few



Scheme 2.9 Copolymerization of ethylene with norbornene [84, 85]

NBE repeat units and contained alternating and/or isolated NBE inserted units due to the difficulty for repeated NBE insertion.

(Indenyl)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2c**) exhibited better NBE incorporation than the Cp*-aryloxo analogue (**2a**), the 1,2,4-Me$_3$C$_5$H$_2$-aryloxo analogue, and the constrained geometry catalyst (CGC, **1**), affording random copolymers with high NBE contents (Scheme 2.9) (Copolymerization with norbornene [84, 85]). The catalytic activity by the indenyl-aryloxo analogue initially increased upon increasing the NBE concentration charged, although the activity generally decreased upon increasing the NBE concentration [84].

The Cp-kemitide analogue, CpTiCl$_2$(N=C^{t}Bu$_2$) (**3a**), exhibits both remarkable activity and efficient NBE incorporation for ethylene/NBE copolymerization [87]. As shown in Table 2.8, the activity increased upon increasing in initial NBE concentration, whereas the activities by other catalysts decreased upon increasing in NBE concentration. Note that the activity by **3a** increased at higher temperature (40, 60 °C) accompanied by increasing NBE content in the copolymer (due to a reduction in ethylene concentration in the mixture), and the activity did not decrease at least for 30 min. The resultant copolymers possessed high molecular weights with unimodal molecular weight distributions as well as with single compositions. The efficient synthesis of high molecular weight copolymers with high NBE contents (58.8–73.5 mol%) could be thus attained upon increasing the NBE concentration at low ethylene pressure (2 atm).

Both the activities and the NBE incorporations in the copolymerization by **3a** were not strongly affected by the Al cocatalyst employed (MAO, MMAOs), and the fact is a unique contrast to that reported in the copolymerization by [Me$_2$Si(fluorenyl)(N^{t}Bu)]TiMe$_2$ in which both the activity and the NBE incorporation are highly dependent upon the Al cocatalyst employed [181–184]. It is thus clear that these observed facts are significantly unique compared to those previously demonstarated in the copolymerization using ordinary metallocenes or linked half-titanocenes (Copolymerization with norbornene [86]).

Table 2.8 Copolymerization of ethylene with norbornene (NBE) by Cp’TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp’=Cp* (**2a**), indenyl (**2c**)], CpTiCl$_2$(N=C^{t}Bu$_2$) (**3a**), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**1**), [Me$_2$Si(indenyl)$_2$]ZrCl$_2$—MAO catalyst systems[a]

Complex (μmol)	Temp/°C	Ethylene /atm	NBE[b] /mmol/mL	Activity[c]	$M_n^d \times 10^{-4}$	M_w/M_n^d	NBE[e] /mol%
Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **2a** (0.2)	25	4	1.0	2640	29.6	1.46	21.7
(Ind)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **2c** (0.2)	25	4	1.0	2300	5.87	1.82	35.2
(Ind)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **2c** (0.2)[f]	25	2	2.5	678	3.91	1.58	58.8
CpTiCl$_2$(N=C^{t}Bu$_2$) **3a** (0.02)	25	4	1.0	40200	71.9	2.92	40.7
CpTiCl$_2$(N=C^{t}Bu$_2$) **3a** (0.02)	40	4	1.0	48900	62.0	2.37	45.9
CpTiCl$_2$(N=C^{t}Bu$_2$) **3a** (0.02)	60	4	1.0	194000	47.5	2.20	51.2
CpTiCl$_2$(N=C^{t}Bu$_2$) **3a** (0.02)[f]	25	2	10.0	31500	44.4	2.01	73.5
[Me$_2$Si(indenyl)$_2$]ZrCl$_2$(0.10)	25	4	1.0	4860	22.9	2.37	29.5
[Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ **1** (0.50)	25	4	1.0	2000	12.8	2.15	26.5

[a] Cited from Ref. [86], *Conditions* toluene + NBE total 50 mL, MAO white solid (prepared by removing AlMe$_3$, toluene from PMAO) 3.0 mmol, 10 min

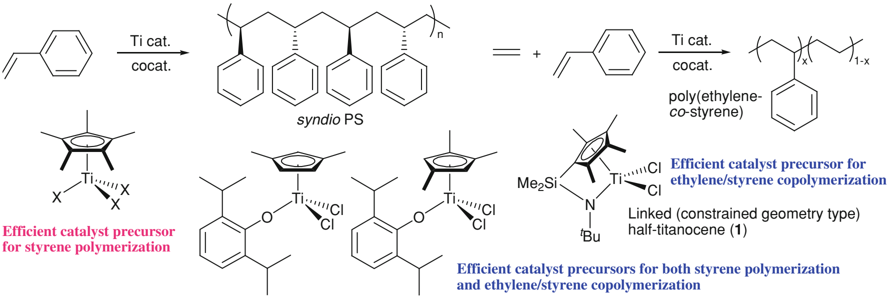
[b] NBE concentration charged (mmol/mL)

[c] Activity in kg-polymer/mol-M·h (M=Ti, Zr)

[d] GPC data in *o*-dichlorobenzene versus polystyrene standards

[e] NBE content (mol %) estimated by ^{13}C NMR spectra

[f] *Conditions* toluene + NBE total 10 mL



Scheme 2.10 Syndiospecific styrene polymerization and ethylene/styrene copolymerization by half-titanocenes [41, 42]

2.3 Syndiospecific Styrene Polymerization and Ethylene/Styrene Copolymerization Using Half-Titanocenes: Ligand Effects and Some New Mechanistic Aspects

Syndiotactic polystyrene (SPS) is a unique polymeric material due to its high melting point (T_m=270 °C), high crystallinity, low density, low dielectric constant, and high chemical resistance toward organic solvents [10, 40, 109, 110, Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187]). This polymer cannot be prepared by free radical, anionic or ordinary Ziegler–Natta processes, but can be prepared by the syndiospecific polymerization using various half-titanocenes (Scheme 2.10), Cp'TiX_3 or Cp'TiX_2(Y) (Cp' = cyclopentadienyl group; X = halogen, alkoxo, alkyl etc.; Y = anionic donor ligand) [10]. Ethylene/styrene co-polymers, which cannot be prepared by conventional (free radical, Ziegler–Natta) processes [10, See Reviews for linked half-titanocenes [16, 41, 42, 188–190]), also attract considerable attention [191–193], because styrene incorporation into the PE backbone results in drastic changes in the viscoelastic behavior as well as in the thermomechanical properties of the polymeric material [192].

Half-titanocenes such as Cp*TiF_3, Cp*$Ti(OMe)_3$ and (indenyl)$TiCl_3$ are known to be efficient catalyst precursors for syndiospecific styrene polymerization ([10, 42, 111, 112, 188–194, Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst 195–197]). However, these catalysts showed low activities in ethylene/styrene copolymerization and the resultant polymers afforded a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E/S copolymer) (Examples in ethylene/styrene copolymerization [194–198]). In contrast, modified half-titanocenes of the type, Cp'TiX_2(Y), are effective for both the styrene polymerization and ethylene/styrene copolymerization to afford the copolymers exclusively (Scheme 2.10) ([41, 42], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90–95]). Linked half-titanocenes (so-called "constrained geometry type") are also effective for the copolymerization (See Reviews for linked half-titanocenes [15–17, 41, 42, 114, 115, 199–209], although these complexes generally exhibited extremely low catalytic activities for the styrene polymerization [199, 208]. Certain metallocenes and group 4 transition metal complexes, so-called post-metallocenes are also known to be effective for the copolymerization [210–216].

2.3.1 Syndiospecific Styrene Polymerization Using Cp'TiX$_2$(Y)–MAO Catalyst Systems

Modified half-titanocenes showed unique characteristics in ethylene copolymerizations (Reviews for nonbridged half-titanocenes [19, 20], Ethylene copolymerization with 2-methyl-1-pentene (disubstited α-olefin [78–80, 82–95]), and it was demonstrated that an efficient catalyst for ethylene polymerization can be modified for efficient catalysts for syndiospecific styrene polymerization by the ligand modification (Cp') ([42], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90]). Figure 2.2 summarizes the results for styrene polymerization using a series of Cp'TiCl$_2$(OAr) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and Cp'TiCl$_3$ [Cp'=Cp, 1,3-Me$_2$C$_5$H$_3$, C$_5$Me$_5$] complexes in the presence of MAO at various temperatures [217]. The activities by Cp'TiCl$_2$(OAr) increased at high temperature, and the activity with 16,000 kg-*s*PS/mol-Ti·h was attained with CpTiCl$_2$(OAr) at 85 °C. The activity at 70 °C increased in the order: Cp > 1,3-Me$_2$C$_5$H$_3$ $\gg$ 1,2,4-Me$_3$C$_5$H$_2$ > C$_5$Me$_5$. The trend was the same as that by Cp'TiCl$_3$, suggesting that the activity was strongly affected by the nature of Cp': the observed trend was similar to that reported by Kaminsky [218]. The M_w values in the resultant SPS prepared by the aryloxo analogues increased in the order: C$_5$Me$_5$ > 1,2,4-Me$_3$C$_5$H$_2$, 1,3-Me$_2$C$_5$H$_3$ > Cp. Although some M_w values were different from those by the trichloride systems, the order in the M_w values was similar to that by the trichloride systems [217]. It thus seems that the introduction of an electron- donating substituent on Cp' was effective in obtainment of high molecular weight SPS [217]. The activity by Cp*TiCl$_2$(Y) was also affected by the anionic donor ligand (Y, Table 2.9) [42, 70, 217, 219, 220], and the activity at 70 °C increased in the order: Y = O-2,6-Me$_2$C$_6$H$_3$ $\gg$ OPh, O-4-MeC$_6$H$_4$, O-2,6-^{i}Pr$_2$C$_6$H$_3$ > Cl, O-2,6-^{t}Bu$_2$C$_6$H$_3$ > O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$ > O-2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$ > N=C^{t}Bu$_2$. The results clearly indicate that the substituent on the aryloxy (anionic donor) ligand *directly affects* the catalytic activity. Moreover, the M_w value for resultant SPS was also dependent upon the anionic ligand employed. These results suggest that aryloxo ligand play an important role toward both the activity and the M_w value.

Ordinary half-titanocenes such as Cp*TiCl$_3$, Cp*Ti(OMe)$_3$, (indenyl)TiCl$_3$ are known to be efficient catalyst precursors for syndiospecific styrene polymerization in the presence of a co-catalyst [10, 40, 109, 110, 218, 221–226] (Fig 2.2). Example concerning syndiospecific styrene polymerization by half-titanocene

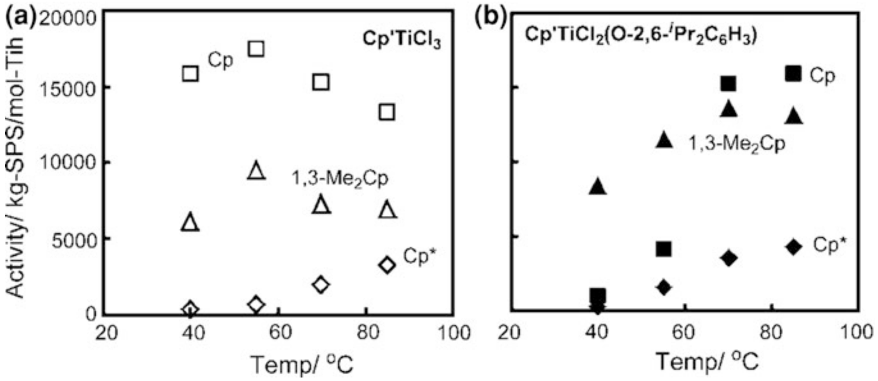


Fig. 2.2 Syndiospecific styrene polymerization by Cp'$TiCl_2$(Y) [Y=Cl or OAr; Ar = 2,6-^{i}Pr_2 C_6H_3]—MAO catalyst systems. ^{a}Cited from Ref. [217], *Conditions* complex 2.0 μmol, styrene/ toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. **a** Cp'$TiCl_3$—MAO catalyst systems; **b** Cp'$TiCl_2$(2,6-^{i}$Pr_2C_6H_3$)—MAO catalyst systems

Table 2.9 Effect of anionic donor ligand in styrene polymerization by Cp*$TiCl_2$(Y)—MAO catalyst systems at 70 °C[a]

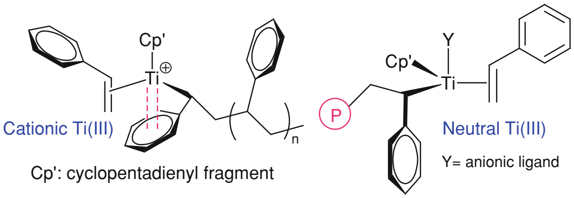
Y (anionic ligand)	Activity[b]	$M_w^c \times 10^{-4}$	M_w/M_n^c
Cl	1970	24.8	2.5
OC_6H_5	4170	54.3	2.0
O-4-MeC_6H_4	3750	26.7	2.4
O-2,6-$Me_2C_6H_3$	9200	28.0	2.1
O-2,6-^{i}$Pr_2C_6H_3$	3600	49.0	2.2
O-2,6-^{t}$Bu_2C_6H_3$	1780	20.5	2.3
O-2-Me-6-{(2,6-^{i}$Pr_2C_6H_3$)N=CH}C_6H_3	552	18.5	2.3
N=C^tBu_2	222	19.1	2.1

[a] Cited from Refs. [70, 217, 219, 220], *Conditions* complex 2.0 μmol, styrene/toluene = 10/ 20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min

[b] Activity in kg-*s*PS/mol-Ti·h

[c] GPC data in *o*-dichlorobenzene versus polystyrene standards

Scheme 2.11 Proposed catalytically-active species for syndiospecific styrene polymerization [38]



complex—borate catalyst [185–187], Examples of a mechanistic studies for styrene polymerization [227–229]). The oxidation state of the active species has been invoked as cationic Ti(III) (Scheme 2.11, left) ([218, 221–226], Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187, 191–193], whereas the cationic Ti(IV) species would play a role for the ethylene/styrene copolymerization ([41], Related publications for synthesis and reactivity of cationic half-titanocene alkyl complexes containing aryloxo ligand [97, 98], [220]). In contrast, Tomotsu (Idemitsu) insisted a possibility that neutral Ti(III) species [226], [Cp'Ti(R)(Y)(styrene)] (Y = anionic ligand), should play a role as the active species (Scheme 2.11, right) [10, 40–42]. On the basis of the above results, it is clear that both Cp' and Y play an essential role for exhibiting high activity and for affording high molecular weight polymer with unimodal molecular weight distribution. Since the role of anionic donor ligand toward both the activity and the molecular weight is present, if the possibility that neutral Ti(III) or cationic Ti(IV) species plays a role for this polymerization.

2.3.2 Ethylene/Styrene Copolymerization Using Half-Titanocenes

Half-titanocenes, Cp^*TiX_3 (X=F, OMe etc.), which are efficient catalyst precursors for syndiospecific styrene polymerization ([10, 40, 109, 110, 218, 221–226], Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187]), afforded a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E/S copolymer) in the ethylene/styrene (co)polymerization (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93], The product distribution and the [194–198]). The product distribution and the activity in (co)polymerization using a $CpTiX_3$–MAO catalyst system is thus highly sensitive to the anionic donor ligand (X=Cl, CH_2Ph, OCH_3, OCH_2Ph etc.), the reaction conditions, the nature of MAO (Examples in ethylene/styrene copolymerization [196, 197]), and the exact mixing sequence and pre-contact time. These factors usually lead to poor reproducibility. $Cp^*Ti(CH_2Ph)_3$–$B(C_6F_5)_3$ afforded E/S copolymer including PE and SPS, and the distributions were dependent upon the polymerization temperature, the pretreatment procedure (Table 2.10) (Examples in ethylene/styrene copolymerization [195]). The resultant copolymer possessed an alternating sequence, and no resonances ascribed to styrene repeating units were seen. However, it seems very difficult to find suitable conditions for the exclusive preparation of E/S copolymer (Table 2.10), and selective co-oligomerization proceeded in the presence of $Cp'TiCl_3$ (Cp'=Cp, Cp*, indenyl)–$B(C_6F_5)_3$ (MAO) catalyst systems under certain conditions [230, 231].

Table 2.10 Ethylene/styrene copolymerization using $Cp^{*}Ti(CH_2Ph)_3–B(C_6F_5)_3–Al^{i}Bu_3$ catalyst[a]

Temp. /°C	Styrene /mol/L	Yield /g[b]	Activity[c]	Composition (wt%)[d]		
				PE	E/S	SPS
0	1.1	0.30	48	>90		
25	0.8	0.45	72	63	22	15
50	0.4	0.35	56	33	58	9
50	1.2	0.49	78	6	72	22
50	2.0	1.00	160	8	20	72
75	0.5	0.35	56	29	41	30

[a] Cited from Ref. [195], *Conditions* $Cp^{*}Ti(CH_2Ph)_3/B(C_6F_5)_3/Al^{i}Bu_3$ = 25/25/25 μmol, ethylene 1 atm, toluene + styrene total 26 mL

[b] After removal of atactic polystyrene

[c] Activity in kg-polymer/mol-Ti·h

[d] Estimated from ^{13}C NMR spectra

Scheme 2.12 Selective linked half-titanocenes for ethylene/styrene copolymerization [129]

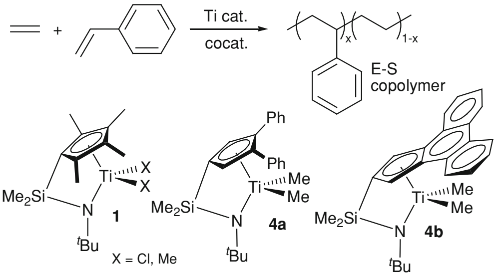


Table 2.11 Copolymerization of ethylene with styrene using different linked half-titanocenes—MAO catalyst systems[a]

Complex	Activity[b]	$M_w^c \times 10^{-4}$	M_w/M_n^c	Styrene[d]/mol%
1 (X=Me)	23700	1.13	2.36	11.0
4a	61000	7.28	4.76	21.5
4b	99400	13.4	5.26	30.6

[a] Cited from Ref. [201], *Conditions* complex 3.0 μmol, styrene 455 g, toluene 433 g, ethylene 200 psi (13.6 atm), H_2 50 psi, $B(C_6F_5)_3$ 3.0 μmol, 90 °C, 30 min

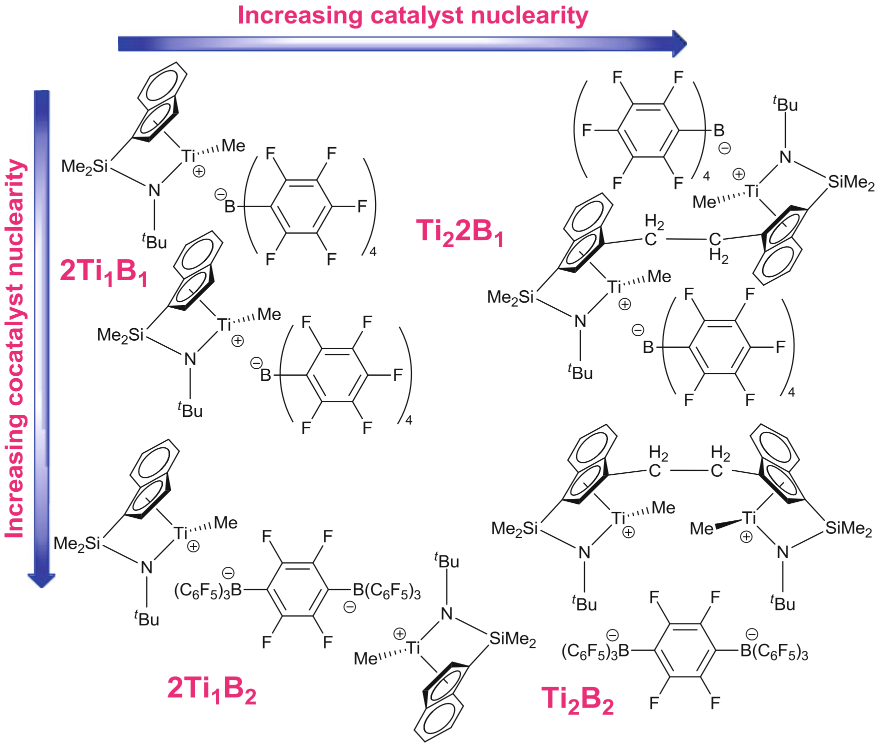
[b] Activity in kg-polymer/mol-Ti·h

[c] GPC data in *o*-dichlorobenzene versus polyethylene standards

[d] Styrene content in E/S copolymer estimated by ^{1}H NMR spectra

2.3.2.1 Recent Results in Ethylene/Styrene Copolymerization by Linked (Constrained Geometry Type) Half-Titanocenes

Linked half-titanocenes like $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**, constrained geometry catalyst, CGC) are known to be efficient catalyst precursors for the copolymerization (Reviews for linked half-titanocenes, see [15–17, 199–207]), although



Scheme 2.13 Catalyst/cocatalyst nuclearity matrix for constrained geometry catalysts [124]

they exhibited extremely low activity for the styrene polymerization [199, 208]. The styrene incorporation is generally invariably <50 gmol%, regardless of the styrene/ethylene feed ratio (Reviews for linked half-titanocenes, see [15–17, 199–207]). It has been known that the cyclopentadienyl fragment affected both the activity and the styrene incorporation [202–204]. The amide substituent was also effective for the styrene incorporation [206, 207], and notable styrene incorporation was attained with [$Me_2Si(C_5Me_4)(NCy)]TiCl_2$ [207]. Complexes **4a**,**b** shown in Scheme 2.12 showed a significantly better efficiency than catalyst 1 (X=Me) (Table 2.11) [201]: **4b** showed better both activity and efficient styrene incorporation than **4a** under the same conditions.

As described above, mononuclear linked half-titanocenes (CGCs) showed extremely low activity for styrene polymerization, and the styrene content in the resultant copolymer did not exceed 50 mol%. In contrast, the bimetallic system (**Ti_22B_1** or **Ti_2B_2** in Scheme 2.13) exhibited significantly higher catalytic activities for styrene polymerization than the mononuclear system (**$2Ti_1B_1$** or **$2Ti_1B_2$**), although the resultant polymer possessed *atactic* stereoregularity (Table 2.12) (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124, 208, 209].

Table 2.12 Styrene polymerization and ethylene/styrene copolymerization catalyzed by mononuclear or dinuclear linked half-titanocenes—cocatalyst systems[a]

Cat.	Styrene/toluene (mL/mL)	Ethylene / atm	Time /h	Activity[b]	$M_w^c \times 10^{-4}$	M_w/M_n^c	Styrene / mol%[d]
Ti$_1$ + B$_1$	5/25	–	3	2.7	11.96	1.84	100
Ti$_2$ + B$_2$	5/25	–	3	104	1.04	1.44	100
Ti$_2$ + B$_1$	5/25	–	3	112	0.80	1.47	100
Ti$_2$ + B$_1$	10/50	1.0	1	259	35.8	1.82	39
Ti$_2$ + B$_1$	20/40	1.0	1.5	194	47.1	1.33	50
Ti$_2$ + B$_1$	30/30	1.0	0.5	384	43.8	2.40	66
Ti$_2$ + B$_1$	60/0	1.0	0.5	312	47.9	1.72	76

[a] Cited from Refs. (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124, 208, 209]), *Conditions* **Ti$_1$** (10 μmol) or **Ti$_2$** (5 μmol) + **B$_1$** (10 μmol) or **B$_2$** (5 μmol), 20 °C, ethylene 1.0 atm

[b] Activity in kg-polymer/mol-Ti·h

[c] By DSC thermograms

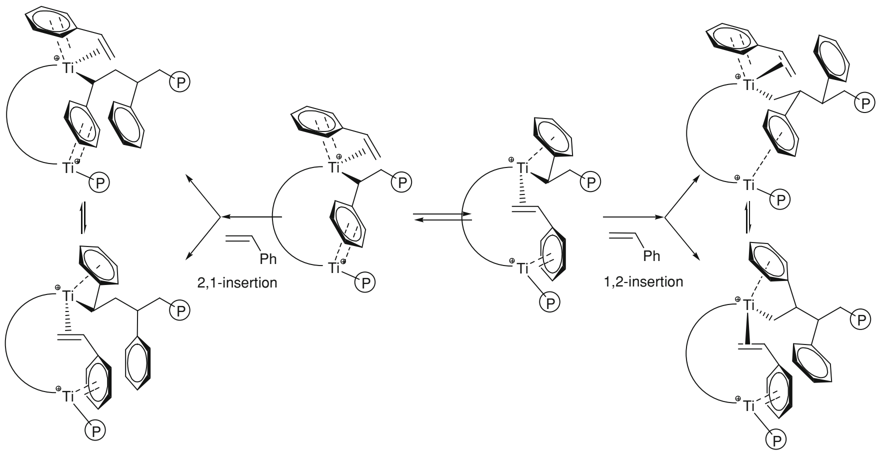
[d] GPC data in *o*-dichlorobenzene versus polystyrene standards

[e] Estimated by ^{13} C NMR spectra

A drastic improvement in the styrene incorporation in the copolymerization could be achieved by using a dinuclear catalyst system (**Ti$_2$2B$_1$**), synthesis of a copolymer with a high styrene content (76 mol%) has thus been achieved in this catalysis (Table 2.12). Although the observed activities should be further improved, this catalyst system afforded broad range controllable styrene incorporation (styrene contents 39–76 mol%) (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124]). Resonances ascribed to the three head-to-tail coupled styrene units in addition to tail-to-tail coupled dyads were observed in the ^{13}C NMR spectra of the copolymers (styrene > 50 mol%) [208]. It was assumed that the arene ring of the last-inserted styrene may preferentially coordinate to the adjacent Ti center in the bimetallic **Ti$_2$** (Scheme 2.14), thus reducing coordinative saturation at the polymerization site and accelerating homopolymerization (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124], 218]. The coordinated arene rings can, in principle, participate in several types of multimetallic/enchainment-altering interaction.

2.3.2.2 Ethylene/Styrene Copolymerization by Modified Half-Titanocenes, Cp'TiX$_2$(Y)

The aryloxo modified half-titanocenes, Cp'TiX$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (X=Cl, Me) exhibited high catalytic activities for ethylene/styrene copolymerization in the presence of MAO, affording poly(ethylene-*co*-styrene)s exclusively without PE and/or SPS as by-products (Table 2.13) (Copolymerization with styrene with



Scheme 2.14 Proposed pathways in the ethylene/styrene copolymerization [124]

Table 2.13 Ethylene/styrene copolymerization by Cp'$TiCl_2$(OAr) [Cp'=1,2,3-$Me_3C_5H_2$, 1,3-$Me_2C_5H_3$, *tert*-BuC_5H_4; OAr=O-2,6-$^iPr_2C_6H_3$] or [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$–MAO catalyst systems[a]

Complexes	Styrene / mL	Activity[b]	E/S copolymer (THF soluble)			
			content[c] / wt%	M_w[d] × 10^{-4}	M_w/ M_n[d]	Styrene / mol%[e]
(1,2,3-$Me_3C_5H_2$)$TiCl_2$(OAr)	3	4100	99.1	17.0	1.6	26.0
(1,2,3-$Me_3C_5H_2$)$TiCl_2$(OAr)	5	3070	98.3	11.0	1.7	38.8
(1,2,3-$Me_3C_5H_2$)$TiCl_2$(OAr)	10	2720	97.8	6.6	1.6	51.2
(1,2,3-$Me_3C_5H_2$)$TiCl_2$(OAr)[f]	15	1850	90.4	3.6	2.1	73.6
(1,3-$Me_2C_5H_3$)$TiCl_2$(OAr)	10	4140	98.2	3.7	1.6	49.0
($^tBuC_5H_4$)$TiCl_2$(OAr)	10	1840	98.7	3.5	2.2	51.2
[$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$	10	5630	99.6	18.0	1.8	32.7

[a] Cited from Ref. [91], *Conditions* complex 1.0 μmol (2.0 μmol/mL-toluene), ethylene 4 atm, total volume of toluene and styrene = 30 mL, MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min

[b] Activity in kg-polymer/mol-Ti·h, polymer yield in acetone insoluble fraction

[c] Percentage of content in copolymer based on polymer obtained (acetone insoluble, THF soluble fraction)

[d] GPC data in *o*-dichlorobenzene versus polystyrene standards

[e] Styrene content (mol%) in copolymer by ^{1} H NMR (1,1,2,2-$C_2D_2Cl_4$)

[f] Conducted under ethylene 2 atm

efficient styrene incorporation or in a living manner [90, 91]). The resultant copolymers possessed not only relatively high molecular weights with unimodal molecular weight distributions, but also single composition as confirmed by DSC thermograms, CFC and GPC/FT-IR (Copolymerization with styrene with efficient styrene incorporation or in a living manner [91]). The activities decreased slightly with an increase in the styrene concentration, whereas the styrene contents in the copolymers increased upon increasing the [S]/[E] initial feed molar ratios. Styrene incorporations with aryloxo analogues is more efficient than that with $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**, X=Cl). Thus, the present catalysis provides an efficient synthesis of copolymer with high styrene content, especially higher than 50 mol%, in a random manner. The microstructure analysis in the resultant E/S copolymers by ^{13}C NMR spectra indicated that the copolymer prepared by $(1,2,3\text{-}Me_3C_5H_2)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ possesses resonances ascribed to two or three styrene repeat units connected via head-to-tail coupling, in addition to the resonances ascribed to tail-to-tail coupling of a styrene unit or head-to-head bridged by an intervening ethylene unit. This is especially interesting in contrast to the results with the linked half-titanocene (**1**) ([40], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90, 91]).

The copolymerization by $Cp^*TiCl_2(N{=}C^tBu_2)$ (**3b**) took place in a living manner in the presence of MAO co-catalyst, although the homopolymerization of ethylene and styrene did not proceed in a living manner [92]. No styrene repeating units were observed in the resultant copolymers, suggesting that a certain degree of styrene insertion inhibits chain transfer in this catalysis. The living nature was maintained under various conditions (Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93]). Copolymerization with $CpTiX_2(N{=}PCy_3)$ (**5**, X=Cl, Me)-cocatalyst (MAO, borates) systems proceeded with notable catalytic activities [at 60–90 °C, ethylene 70 psi (4.76 atm), $[S]/[E] = 12$] [76], however, the styrene incorporation seemed less efficient than with either aryloxo analogues or linked half-titanocene [styrene content: 33.4–61.4 wt% (<27.6 mol%)] [76, 232].

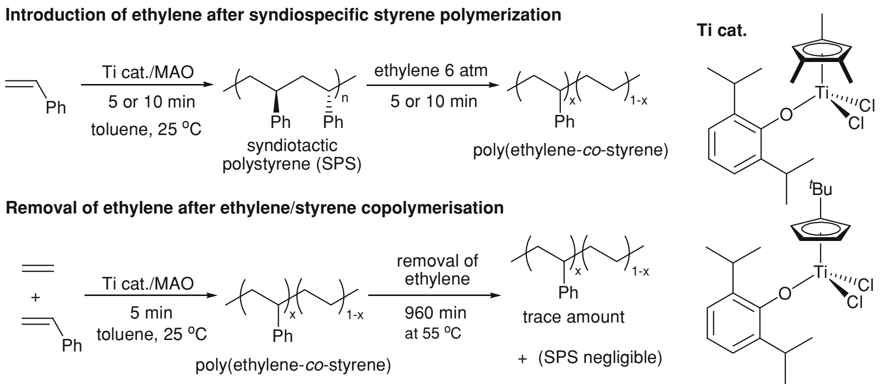
Taking into account the above results, it is clear that modified half-titanocenes, $Cp'TiX_2(Y)$, are better catalyst precursors for synthesis of ethylene/styrene copolymers in high yields. It was also clear that both the activity and the styrene incorporation are dependent upon the type of ligands employed (Cp' and Y). These complexes are also effective for not only ethylene polymerization, but also syndiospecific styrene polymerization: the results are in unique contrast to those with ordinary half-titanocenes, $Cp'TiX_3$. Therefore, these catalysts may be suitable for mechanistic study on syndiospecific styrene polymerization as well as copolymerization, as described below ([41], Copolymerization with styrene with efficient styrene incorporation or in a living manner [93, 94]).

2.3.3 Role of Anionic Donor Ligand in Ethylene/Styrene Copolymerization and Syndiospecific Styrene Polymerization: Mechanistic Considerations

Ethylene/styrene copolymerizations using three half-titanocenes containing Cp* ligand of type, $Cp^*TiX_2(Y)$ [X=Cl, Y=O-2,6-^{i}$Pr_2C_6H_3$, Cl; X=Me, Y=O-2,6-^{i}$Pr_2C_6H_3$, Me]—cocatalyst systems were used under the same conditions [93]. The copolymerizations with $Cp^*TiCl_2(OAr)$ (**2a**) gave copolymers with high styrene contents (31.9–34.3 mol%), and significant increase in the activity was not observed at high temperature. The resultant copolymers prepared by **2a** possessed lower M_n values with unimodal distributions ($M_w/M_n = 1.50$–1.62). In contrast, the polymers prepared with the trichloride analogue, Cp^*TiCl_3, showed bimodal molecular weight distributions consisting of a mixture of PE and SPS, and the proportion of SPS increased at high temperature due to an increase in the activity for syndiospecific styrene polymerization (for syndiospecific styrene polymerization [91, 217]). Copolymerization using the aryloxy-dimethyl analogue, $Cp^*TiMe_2(OAr)$–MAO or $[PhN(H)Me_2][B(C_6F_5)_4]$ (AFPB) catalyst system afforded the copolymer exclusively [93]. In contrast, the polymer prepared with the Cp^*TiMe_3-AFPB catalyst was PE (containing a trace amount of the copolymer with low styrene content) or the copolymer with an extremely low styrene content, whereas the copolymerization in the presence of MAO afforded a mixture of PE and SPS, as observed in the (co)polymerization using Cp^*TiCl_3. The fact that no SPS was formed in polymerization with Cp^*TiMe_3–AFPB catalyst was analogous to the fact that $Cp^*Ti(CH_2Ph)_3$–AFPB catalyst did not afford SPS in an attempted styrene polymerization (under dark conditions), and only poly(propylene-*co*-styrene) oligomer was formed in the propylene/styrene copolymerization [227–229].

These results strongly suggest that cationic Ti(IV) species play an important key role in the ethylene polymerization as well as the ethylene/styrene copolymerization. These results also suggest that another catalytically-active species [likely Ti(III)] for syndiospecific styrene polymerization is formed in the presence of MAO (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93]).

Exclusive formation of copolymers without formation of SPS as a by-product was observed with the introduction of ethylene into a solution of syndiospecific styrene polymerization using Cp'$TiCl_2$(O-2,6-^{i}$Pr_2C_6H_3$) (Cp'=^{t}BuC_5H_4, 1,2,4-$Me_3C_5H_2$)—MAO catalysts (Scheme 2.15). Note that the activities and the M_w values as well as the styrene contents in the latter copolymerizations were identical to those in their independent runs. These results clearly indicate that the active species for the syndiospecific styrene polymerization can be tuned to the active species for copolymerization [94, 233]. In contrast, styrene polymerization did not proceed when ethylene was removed from the reaction mixture of ethylene/styrene copolymerization (likely due to oxidation upon exposure to ethylene) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [94]) (Table 2.14).



Scheme 2.15 Step (co)polymerization of ethylene with styrene [94]

Table 2.14 Copolymerization of ethylene with styrene by $Cp^*TiCl_2(Y)$ [Y=O-2,6-$^iPr_2C_6H_3$ (OAr), Cl]—MAO catalyst systems[a]

Complex Y	Temp. /°c	Composition[b] (%)			Activity[c]	Styrene Cont.[D]/Mol%	$M_n^e \times 10^{-4}$	M_w/M_n^e
		E-S	PE	SPS				
OAr	25	>99	tr.	tr.	504	31.9	9.28	1.62
OAr	40	>98	tr.	tr.	660	34.3	9.79	1.50
Cl[f]	25	tr.	86.8	13.2	250	>99 [g]	5.85	1.26
						–	0.29	2.69
Cl[f]	40	tr.	81.6	18.4	280	>99 [g]	5.07	1.31
						–	0.31	1.75
Cl[f]	55	tr.	69.8	30.2	260	>99 [g]	3.56	1.48
						–	0.21	1.77

[a] Cited from Ref. [93], *Conditions* catalyst 2.0 μmol, MAO white solid 3.0 mmol, ethylene 6 atm, styrene 10 mL, styrene + toluene total 30 mL, 10 min

[b] Based on a mixture of PE, SPS and copolymer. (acetone insoluble fraction)

[c] Activity in kg-polymer/mol-Ti·h

[d] Styrene content (mol%) estimated by ^{1}H NMR spectra

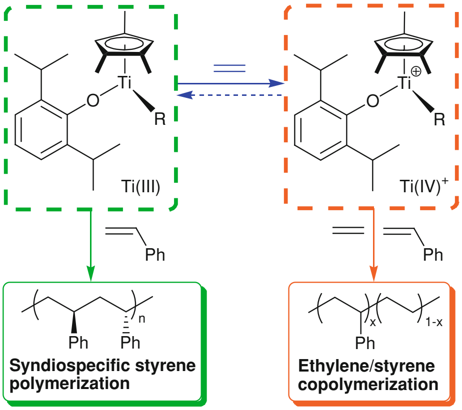
[e] GPC data in *o*-dichlorobenzene versus polystyrene standards.

[f] Resultant polymers were a mixture of PE and SPS

[g] Confirmed by GPC/FT-IR, ^{13}C NMR spectra, DSC thermograms

Taking the results into account [93], it seems likely that the cationic Ti(IV) species, $[Cp'Ti(L)R]^+$, play a role in the copolymerization and the active species containing an anionic ancillary donor ligand [assumed to be neutral Ti(III), Cp'Ti(L)R] proposed by Tomotsu et al. [226] plays a role in the syndiospecific styrene polymerization (Scheme 2.16) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [94]). These results should also explain the reported findings that the activities and molecular weight of the resultant syndiotactic polystyrene in styrene polymerization using

Scheme 2.16 Proposed catalytically-active species for syndiospecific styrene polymerization and ethylene/styrene copolymerization [41, 93]



Cp’TiX$_2$(Y)—cocatalyst systems were highly dependent upon the anionic donor ligand (Y) [93, 94, 233]. These proposals are in contrasts to the hypothesis that cationic Ti(III) species, [Cp’Ti(R)(styrene)]$^+$, play a role as the catalytically-active species for the styrene polymerization using Cp’TiX$_3$. This hypothesis should help to explain why polystyrene structures in the resultant copolymers prepared with Cp’TiCl$_2$(Y)—MAO catalysts are atactic.

2.4 Summary and Outlook

As described above, it is now clear that *nonbridged* modified half-titanocenes containing anionic ancillary donor ligand of the type, Cp’TiX$_2$(Y), displayed unique characteristics that are different from those especially by ordinary catalysts (Ziegler-Natta, metallocenes, linked half-titanocenes). Ligand modifications (Cp’, Y) are very important especially for the successful copolymerizations (with both remarkable activities and efficient comonomer incorporation) [19, 20]. As demonstrated above (Copolymerization with styrene with efficient styrene incorporation or in a living manner, [90]). Equilibrium constants for alkene coordination to (MeC$_5$H$_4$)$_2$Zr$^+$(O$^{t\text{-}}$Bu)(ClCD$_2$Cl) [167], See For reported examples of insertion of vinyltrimethylsilane into cationic zirconium complexes [168–171], the efficient catalyst precursors for ethylene polymerization can be tune to the efficient catalyst precursors for syndiospecific styrene polymerization by simple modification of cyclopentadienyl fragment: this is one of the unique characteristics for using this catalysis. Fine tuning of anionic donor ligand is also important for exhibiting high (with better stability in the catalytic reaction) as well as with better comonomer incorporation. Several promising findings that should be very important from both academic and industrial viewpoints have been demonstrated, and these efforts will pave new promising possibilities for evolution of new *fine* polyolefins with unique properties by incorporation of new comonomers and/or by adopting new synthetic strategies.

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233. However, this switch by the Cp'-aryloxy analogues were dependent upon the cyclopentadienyl fragment (Cp'), the polymerization temperature, styrene/ethylene molar ratio, and SPS was accompanied under certain conditions [94]. The fact would also support the proposed equibrium shown in Scheme 2.15 [94]
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Chapter 3
Olefin Polymerization with Non-metallocene Catalysts (Early Transition Metals)

Kotohiro Nomura and Wenjuan Zhang

Abstract In this chapter, recent developments of so called non-metallocene early transition metal (group 3–5) complexes as the catalyst precursors for olefin polymerization have been described. These catalysts display unique characterisitics especially for ethylene (co)polymerization, and high isospecificity ([*mmmm*] $> 99.6\ \%$) in propylene polymerization has been achieved in some catalyses. The ligand modification plays an essential key role not only for the catalytic activity, but also for control of tacticity and/or living nature in these catalyses.

3.1 Introduction

After a discovery of so called metallocene catalysts [Cp_2ZrCl_2—methylaluminoxane (MAO) catalyst] by Kaminsky et al. [1, 2], many researchers focused on design and synthesis of bridged (*ansa*) metallocene (see Reviews for metallocenes [3–6]; *Frontiers in Metal-Catalysed Polymerization* (special issue) [7–10]) and half-titanocene complex (exemplified as constrained geometry catalyst, CGC) (see Reviews for linked half-titanocenes [11–13]) for efficient ethylene/α-olefin copolymerization and isospecific polymerization of α-olefins. Nonbridged (unbridged) half-titanocene catalysts (see Reviews for nonbridged half-titanocenes [14–17]), described in Chap. 2, may also be considered as the related stream, although the basic concept in the catalyst design is somewhat different. In olefin polymerization using metallocene catalysts, it has been postulated that the cationic alkyl species, Cp_2Zr^+R, play an essential key role as the active species [3–6]. Therefore,

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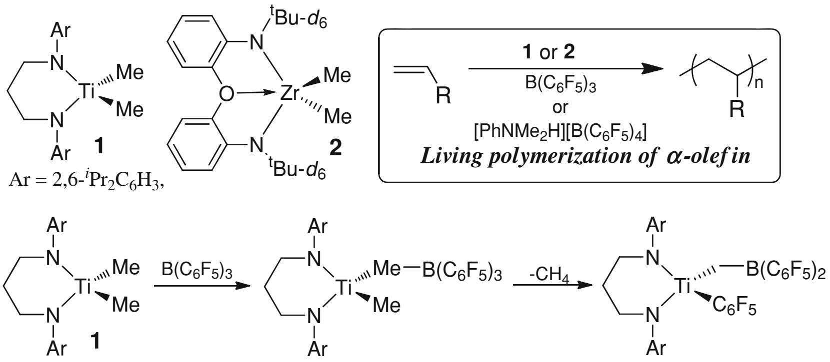
researchers only focused on generating 14e species from the catalyst precursor. Later it has been well known exemplified as $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC) that 12e species also plays a role, suggesting many promising possibilities for designing efficient catalysts with various ligand. After a report concerning 1-hexene polymerization using a titanium complex containing bis(amide) ligand as the catalyst precursor by Dr. McConville [18, 19], described below, many researchers from both academic and industry invloved in the project for exploring a possibility with various early transition metals. Nowadays, tremendous number of reports have been known for this project, and some of them are very important from both academic and industrial point of view (see Reviews for post-metallocenes [20–24]; *Metal-catalysed Polymerisation* (*special issue*) [25]; Selected reviews for living polymerization [26–28]). In this chapter, efforts for designing molecular catalysts with early transition metals have been briefly reviewed.

3.2 Design, Synthesis of Molecular Catalyst with Early Transition Metals

3.2.1 Titanium, Zirconium, and Hafnium Complexes

As described above, titanium complex (**1**) containing bis(amide) ligand [18, 19] and zirconium complex with tridentate diamido ligand, $[NON]ZrMe_2$ (**2**) [29], for 1-hexene living polymerization introduced promising possibility for designing efficient catalyst, which does not contain cyclopentadienyl ligand (called non-metallocene catalyst), for olefin polymerization (Scheme 3.1). The catalytic activities by **1** in 1-hexene polymerization were suppressed upon addition of toluene, suggesting a possibility of coordination of toluene to the cationic catalytically-active species. Reaction of **1** with $B(C_6F_5)_3$ in *n*-pentane gave insoluble yellow-orange solids that was considered as a true catalyst for the living polymerization. The pentane suspensions slowly evolved CH_4 over several hours to give the pentane-soluble $[ArN(CH_2)_3NAr]Ti[CH_2B(C_6F_5)_2](C_6F_5)$, which was structurally characterized and was inactive for the polymerization of α-olefins [30]. The resultant poly(1-hexene)s prepared by **1**, **2** possessed atactic stereoregularity.

Although the resultant polymer in the above reports afforded atactic poly (1-hexene), Eisen et al. presented synthesis of isotactic polypropylene by zirconium complexes containing tris(amidinate) ligand with chiral *N*-substituents, $[N(R^*)\text{-}C\text{–}N]_3ZrCl$ (**3**) [31]. In the propylene polymerization by **3**—MAO catalyst in toluene, isotacticities for the resultant polymers were dependent upon the propylene pressure; the attempt under the atmospheric pressure of propylene was not successful. They speculated that one ancillary ligand was not acting as a spectator ligand, and MAO extracted one benzamidinate ligand from **3**. This



Scheme 3.1 Pioneering examples for living 1-hexene polymerization [18, 19, 29]

displacement reaction would afford the proposed catalytically active species **3′**. Isospecific propylene polymerization took place if zirconium complexes containing bis(amidinate) complexes (**4**), bearing achiral substituents R, at higher propylene pressures [32]. As shown in Table 3.1, the stereo-regularity in the resultant polypropylene was modulated by the pressure (from atactic to isotactic through elastomers). The different effects in the polymerization process such as the nature of solvent or cocatalyst, temperature, pressure, Al/M molar ratio (M = Ti, Zr), and the relationship between the symmetry of the complex and the polymer microstructure had been investigated [34]. The stereoregular errors were formed by the intramolecular epimerization of the growing chain at the last inserted unit. It was thus proposed that epimerization becomes faster than the stereoregular insertion of propylene at lower propylene pressure, leading to the formation of atactic polymer [34] (Scheme 3.2).

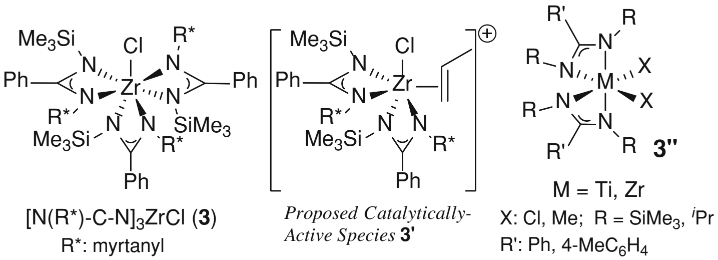
Isospecific living polymerization had been achieved by using C_2 symmetrical zirconium complex containing chelate bis(phenolate) ligand (**4b**, Scheme 3.3) [35]. Upon activation of **4b** with B(C_6F_5)$_3$, 1-hexene polymerization took place (rather efficiently), affording poly(1-hexene) with narrow molecular weight distribution (18 kg-polymer/mol-Zr·h, M_w = 12000, M_w/M_n = 1.15, >95 % isotacticity). It was thus assumed that the high isotacticity would be due to a steric bulk of the ^{t}Bu group in **4b**, because the polymerization by **4a** under the same conditions afforded atactic poly(1-hexene) with higher activity (35 kg-polymer/mol-Zr·h, M_w = 23000, M_w/M_n = 1.57) [35]. The chloride analogue (**4c**) showed remarkable activity (5400 kg-polymer/mol-Zr·h), but the polymerization did not take place in a living manner, suggesting that the electronic factor on the phenyl group plays a role for exhibiting the high activity. In contrast, the titanium analogue of **4c** showed relatively high activity (200 kg-polymer/mol-Ti·h), affording ultra high molecular weight poly(1-hexene) with low PDI value as well as with relatively high isotacticity (M_w = 5.50–19.0 × 10^5, M_w/M_n = >1.2, mm = 60 %) [36].

Titanium and zirconium complexes containing amine bis(phenolate) ligand (**5**) showed remarkable catalytic activity for α-olefin polymerization (Scheme 3.3)

Table 3.1 Propylene polymerization by $[Me_3SiNC(4\text{-}MeC_6H_4)NSiMe_3]_2ZrMe_2$ (**3″**)[a]

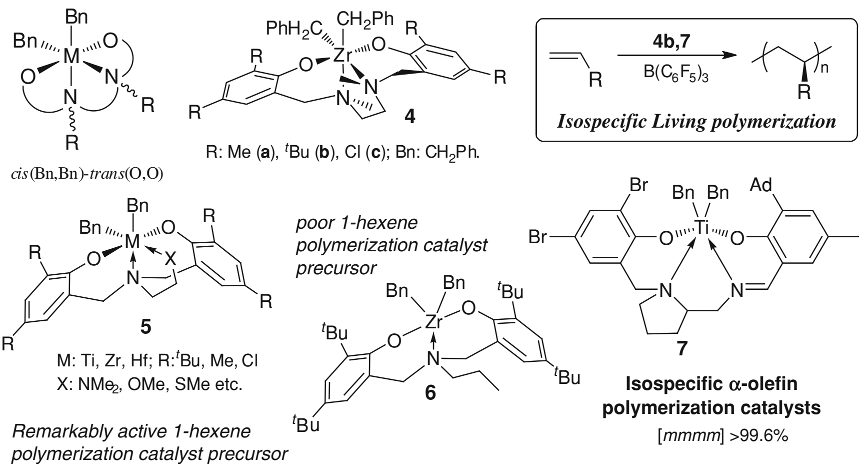
Solvent	Al/Zr[b]	Temp. /°C	Propylene /atm	Activity[c]	M_n^d $\times 10^{-3}$	M_w/M_n^d	*mmmm*[e] /%	T_m^f /°C
Toluene	250	25	9.2	110[g]	261	1.69	86	142
					36.0	2.35	11	oil
CH_2Cl_2	250	25	9.2	220	10.7	2.49	90	146
CH_2Cl_2	400	25	9.2	750	23.5	1.81	96	147
CH_2Cl_2	1000	25	9.2	790	58.1	1.42	98	149
CH_2Cl_2	250	0	5.1	50	10.2	1.85	86	138
CH_2Cl_2	250	25	9.2	220	10.7	2.49	90	146
CH_2Cl_2	250	50	17	2660	150	1.81	96	152
Toluene	$B(C_6F_5)_3$	25	9.2	280[h]	26.0	1.96	98	154
					3.00	3.1	7	oil

[a] Cited from Ref. [34]
[b] MAO (solvent removed from a 20 % solution in toluene)
[c] Activity in kg-PP/mol-Zr·h
[d] GPC data 1,2,4-trichlorobenzene versus polystyrene standards
[e] Estimated by ^{13} C NMR spectra
[f] Melting Temperature
[g] Mixture of isotactic (50 %) and atactic (50 %) fractions of polypropylene
[h] 70 % atactic and 30 % isotactic



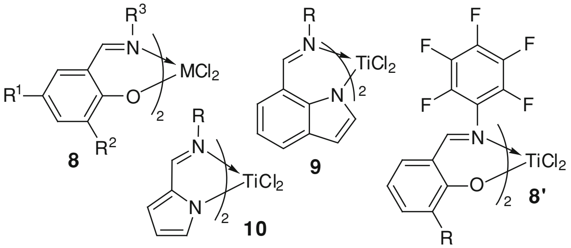
Scheme 3.2 Isospecific propylene polymerization catalysts [31–34]

[36], and the reaction by the titanium analogue (R = ^{t}Bu, X = OMe) proceeded in a living manner, affording block copolymer consisting of poly(1-hexene) and poly(1-octene). An extra arm donor ligand plays an essential role to exhibit high catalytic activity, because the activity with the zirconium analogue (**6**) was extremely low [37]. This may be due to the fact that **6** folds pseudo-trigonal bipyramidal geometry whereas the complexes **5** fold distorted octahedral geometry around the metal center, which lead to the different bond angles between two benzyl (Bn) group (117.4° in **6** and 93.7° in **5**) [37]. More recently, Kol demonstrated that octahedral C_1-symmetric titanium catalysts containing salalen ligand (**7**) are highly effective for isospecific propylene polymerization to afford polymers with extraordinary high isotacticity with high melting transition temperature ([*mmmm*] > 99.6 %, T_m = 169.9 °C) [43].



Scheme 3.3 Group 4 metal complexes containing amine bis(phenolate) ligands [35–43]

Scheme 3.4 Ti, Zr, Hf complexes containing salicylaldiminato ligands



Zirconium complexes bearing two salicylaldiminato-type ligands (**8** in Scheme 3.4) exhibited remarkable catalytic activities for ethylene polymerization [44]. As shown in Table 3.2, the activity and the molecular weight of the polymer were dependent upon the substituent on the ligand. The activity was also affected by the centered metal [45], and increasing the steric bulk especially on both the phenoxy group in *ortho* position and the imino group strongly affected the catalytic activity. Molecular weights in the resultant PE were varied by the ligand modification [44]. The zirconium complex containing *N*-(3-cumyl-5-methyl-salicylidene) cyclohexylaminato ligand showed the highest activity for ethylene polymerization (4315000 kg-PE/mol-Zr·h) at 25 °C.

Importantly, ethylene polymerization by the fluorinated phenoxy-imine analogue (**8′**) proceeded in a living manner [46], and the living polymerization of propylene afforded polypropylene with highly syndiotactic steroregularity [47, 48]. These living polymerizations took place even at room temperature, and synthesis of various block copolymers has been achieved in this catalysis [46–48]. The catalytic activity in the ethylene polymerization was high [46], whereas the activity for propylene polymerization was moderate but the polymerization

Table 3.2 Selected results for ethylene polymerization by Zr complex (**8**)—MAO catalyst systems[a]

Complex R¹, R², R³	Amount /μmol	Activity[b]	$M_v \times 10^{-4}$	M_w/M_n[c]
H, ${}^tBu$, Ph	0.02	550000	0.9	2.06
Me, ${}^tBu$, Ph	0.02	331000	0.7	2
H, Me, Ph	5	400	0.3	2.31
H, ${}^iPr$, Ph	5	900	0.6	2.48
Me, adamantyl, Ph	0.02	714000	1.2	2.69
Me, cumyl, Ph	0.01	2096000	1.8	7.2
Me, cumyl, cyclohexyl	0.005	4315000	1.5	1.88
H, ${}^tBu$, 2-MeC_6H_4	0.5	40000	32	2.13
H, ${}^tBu$, 2-${}^iPrC_6H_4$	0.5	58000	113	2.61
H ${}^tBu$ 2-${}^tBuC_6H_4$	5	100	>274[d]	[e]
H, ${}^tBu$, 3,5-${}^tBu_2C_6H_3$	0.1	244000	2.6	1.79
H, ${}^tBu$, 4-${}^tBuC_6H_4$	0.1	271000	0.7	2.03
H, ${}^tBu$, 2,6-${}^iPr_2C_6H_3$	5	trace		
Me, adamantyl, 2-${}^iPrC_6H_4$	0.1	23000	153	[e]
cumyl, cumyl, 2-${}^iPrC_6H_4$	0.2	43000	220	[e]

[a] Data cited from Ref. [44], Conditions: 25 °C, ethylene 1 atm, MAO (Al) 1.25 mmol, toluene 250 mL, 5 or 30 min

[b] Activity in kg-PE/mol-Zr·h

[c] Measured by GPC

[d] Obtained from the polyethylene soluble in decalin under intrinsic viscosity measurement conditions

[e] Polymer was hardly soluble in *o*-dichlorobenzene under GPC measurement conditions

proceeds in a highly syndiospecific manner although these Ti complexes possess C_2 symmetry [47, 48]. In ethylene polymerizations using titanium complexes with various fluorine containing phenoxy-imine chelate ligands, the complexes having a fluorine atom adjacent to the imine nitrogen showed the living nature at 50 °C, whereas the complexes possessing no fluorine adjacent to the imine nitrogen afforded polyethylenes having M_w/M_n values of ca. 2 with β-hydrogen transfer as the main termination pathway. In addition to the DFT calculation results, they assumed that the presence of a fluorine atom adjacent to the imine nitrogen is the requirement for the high-temperature living polymerization, because the fluorine of the active species for ethylene polymerization interacts with a β-hydrogen in the polymer chain, resulting in the prevention of β-hydrogen transfer [46].

Based on ^{13}C NMR studies, they proposed that syndiotacticity in the propylene polymerization was governed by a chain-end control mechanism and that the polymerization is initiated exclusively via 1,2-insertion followed by 2,1-insertion as the principal mode of polymerization, and that the polypropylenes produced with the Ti complexes possess regio-block structures. Substitutions on the phenoxy-imine ligands affected both the catalytic activity and the stereo specificity, and the steric bulk of the substituent in *ortho* position of the phenoxy oxygen plays a decisive role in achieving high syndioselectivity for the chain-end controlled

Table 3.3 Selected results for propylene polymerization by **8′**—MAO catalyst systems[a]

R in **8′**	Temp./ °C	TOF[b]	$M_n^c \times 10^{-3}$	M_w/M_n^c	T_m^d/ °C	rr^e
H	25	729	189	1.51	nd[f]	
Me	25	1635	260.2	1.22	nd[f]	
^{i}Pr	25	739	153.7	1.16	nd[f]	
^{t}Bu	0	68	23.6	1.05	136	
^{t}Bu	25	87	28.5	1.11	137	87
^{t}Bu	50	70	16.4	1.37	130	
$SiMe_3$	0	72	24.7	1.08	156	94
$SiMe_3$	25	139	47	1.08	152	93
$SiMe_3$	50	113	35.1	1.23	149	90
$SiEt_3$	0	42	11.9	1.08	152	93
$SiEt_3$	25	83	24.4	1.16	151	
$SiEt_3$	50	63	20.4	1.23	148	

[a] Cited from Ref. [48], Conditions: complex 10 μmol, MAO 2.5 mmol, propylene 1 atm, 5 h

[b] Turnover frequency

[c] Determined by GPC using polypropylene calibration

[d] Melting temperature of produced PP determined by DSC

[e] Estimated by ^{13}C NMR spectra

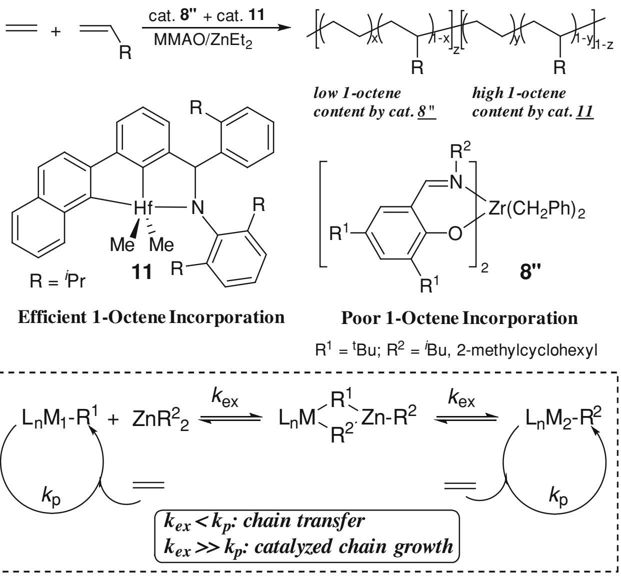
[f] Not detected

polymerization (Table 3.3) [47, 48]. The Ti complex having $SiMe_3$ group in *ortho* position of the phenoxy ligand afforded highly syndiotactic, nearly monodisperse polypropylenes (94–90 % *rr*) with extremely high melting temperatures (T_m = 156–149 °C). The polymerization behavior of the Ti complexes was explained by the proposed chain-end controlled, site-inversion mechanism for the formation of syndiotactic polypropylene by **8′**. Copolymerization of ethylene with α–olefin by **8′** also proceeded in a living manner in the presence of MAO, and various block copolymers were also thus prepared [49].

Synthesis of the related complexes such as titanium complexes containing two indole-imine ligands (**9**) [50], pyrrolide-imine ligand (**10**) were known [51], and living copolymerization of ethylene with norbornene took place if **10** was used as the catalyst precursor [52, 53].

Chain Shuttling Polymerization

Precise synthesis of microblock ethylene/1-octene copolymers which possesses two compositions (copolymers with low/high 1-octene contents) in a polymer chain was also achieved by adopting the polymerization process called "Chain Shuttling Polymerization" in the presence of two catalysts (with efficient/inefficient comonomer incorporations, different monomer reactivity, Scheme 3.5) and chain transfer reagent (Et_2Zn etc.) [54]. The resultant polymers (prepared by adding Et_2Zn during polymerization results in a block copolymer microstructure with intimately mixed interchain hard and soft segments) possess higher transparency than the polymers with two physical blend of high- and low-density polymers, and possessed higher melting temperature and low glass transition temperature (due to a



Scheme 3.5 Precise synthesis of microblock copolymers by "chain shuttling polymerization" [54]

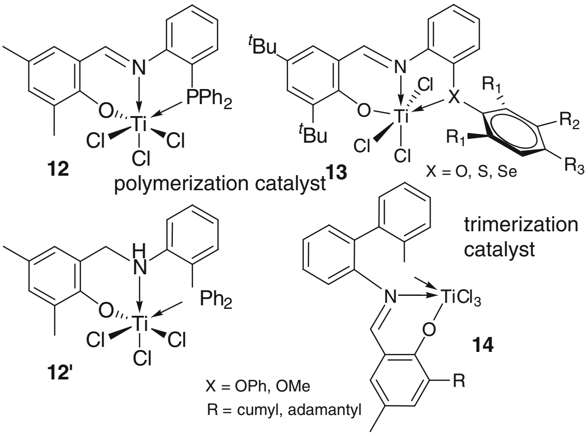
block segment with low 1-octene content). These are recognized as a new technology for evolution of new polymers on the basis of precise olefin polymerization technique [54].

The isospecific α-olefin polymerization catalyst (**11**) was developed by DOW on the basis of 1600 catalyst screenings (required only for 3 weeks) by using "high throughput screening" (Symyx Technologies) technique: this demonstrated a new methodology for the catalyst development [55, 56]. Another key issue on this process is adopting rapid chain transfer reactions enabled by presence of Et_2Zn (rapid chain transfer by Et_2Zn [57–60]): rapid polymer exchange between **8″** and **11** through Zn afforded the polymers with multiblock (microblock) microstructure.

Ligand Modification from Ethylene Polymerization Catalyst to Trimerization Catalyst

It has been known in that ethylene polymerization catalyst was tuned to the ethylene trimerization by the ligand modification. $[(\eta^5\text{-}C_5H_5)CMe_2Ph]TiCl_3$—MAO catalyst exhibited moderate catalytic activity with high selectivity for ethylene trimerization, whereas ethylene polymerization took place by $[(\eta^5\text{-}C_5H_5)CMe_3]$-$TiCl_3$ [61]. Titanium trichloride complexes containing monoanionic tridentate ligands (**12**,**13**) exhibited moderate to high catalytic activities for ethylene polymerization (Scheme 3.6) [62, 64]: **12** showed better catalyst performance for ethylene copolymerization with 1-hexene and norbornene [62]. In contrast, complex **14** showed remarkable selectivity in ethylene trimerization in the presence of MAO, and second order dependence of activity on ethylene pressure (suggesting the metallacycle mechanism) was observed [65]. These would suggest that the

Scheme 3.6 Titanium trichloride complexes for ethylene polymerization/trimerization [62–65]

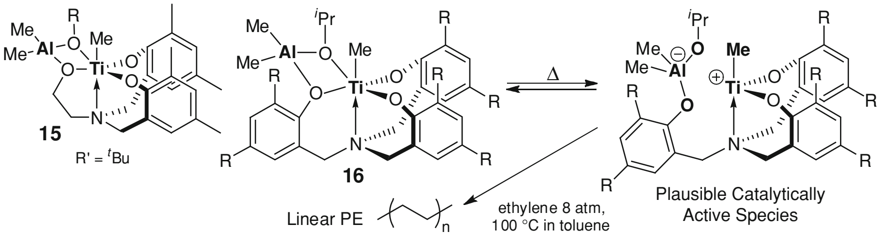


effective catalyst for the polymerization can be tuned to the effective catalyst for the trimerization by the ligand modification.

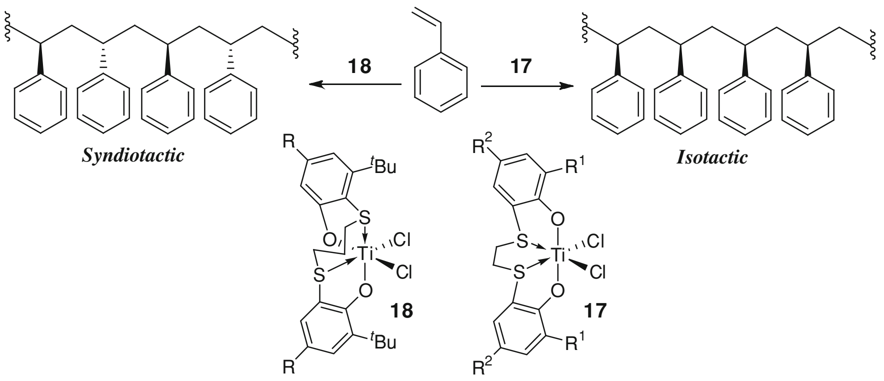
Ti–Al Hetero Bimetallic Complexes Containing Chelate Trianionic Donor Ligand
Titanium complexes with tris(aryloxo)amine or bis(aryloxo)(alkoxo)amine ligand, $Ti(OR')[(O\text{-}2,4\text{-}R_2C_6H_2\text{-}6\text{-}CH_2)_3N]$ or $Ti(OR')[(O\text{-}2,4\text{-}R_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)N]$ ($R = Me$, ${}^tBu$; $R' = {}^iPr$, ${}^tBu$), exhibited from moderate to high catalytic activity for ethylene polymerization especially at high temperature (100–120 °C), and the activities increased upon addition of small amount of $AlMe_3$ [66, 68]. The resultant polymers possessed unimodal molecular weight distributions, suggesting that the polymerization proceeded with a uniform catalytically-active species. The resultant heterobimetallic Ti–Al complexes (**15**, **16**) exhibited moderate catalytic activities upon heating under ethylene pressure even in the absence of any additional cocatalyst, strongly suggesting that cleavages of Ti–O bonds would generate the catalytically active cationic species in this catalysis (Scheme 3.7) [67, 68].

Isospecific/Syndiospecific Styrene Polymerization
Titanium complexes containing 1,4-dithiabutane-bridged derivatives (**17**) showed notable catalytic activities affording isotactic polystyrene with unimodal molecular weight distributions, whereas the 1,5-dithiapentane-bridged derivatives (**18**) showed low catalytic activities affording syndiotactic polystyrene (Scheme 3.8) [69]. The analogous zirconium, hafnium complexes of **17** also showed the low catalytic activity to afford isotactic polystyrene, suggesting that C_2-symmetric ligand sphere should play a crucial role for this isospecific polymerization [69, 71].

As shown in Table 3.4, the substituents on the ligand affected the activity and stereoselectivity, and these facts were evidently related to the effect of these substituents on the stereorigidity of the catalyst precursors. Complexes bearing less bulky *ortho*-substituents R^1 in the aromatic ring (H, Me, ${}^iPr$) allowed rapid interconversion on the NMR time scale, while the complexes with bulky groups (${}^tBu$, CMe_2Ph) were stereorigid at temperatures up to 100 °C. Small *ortho*-



Scheme 3.7 Ti-Al Hetero bimetallic complexes that polymerize ethylene without cocatalyst [67, 68]



Scheme 3.8 Isospecific styrene polymerization by titanium complexes containing chelate bis(phenolate) ligands [69–71]

substituents thus led to configurational lability at room temperature and resulted in the loss of both activity and stereospecificity. Syndiospecific styrene polymerization with relatively low activity was observed by titanium complexes with 1,5-dithiapentanediyl-linked bis(phenolato) ligands. Only the configurationally stable 1,4-dithiabutanediyl-linked phenolates with bulky *ortho*-substituents appeared to be capable of stabilizing a C_2-symmetric, helical ligand sphere at the titanium center and thereby provided an active site for the isospecific styrene polymerization [71].

3.2.2 Vanadium Complexes

Classical Ziegler type vanadium catalysts (ex. $VOCl_3$, VCl_4, VCl_3–$AlBr_3$, $AlCl_3$–$AlPh_3$, Al^iBu_3, $SnPh_4$) are known to display unique characteristics in olefin polymerization. In general, these catalyst systems afforded (i) high molecular

Table 3.4 Isospecific/syndiospecific styrene polymerization by titanium complexes containing chelate bis(phenolate) ligands[a]

Complex	Substituents: R^1, R^2	Activity[b]	$M_n^c \times 10^{-4}$	M_w/M_n^c	T_m^d/°C
17[e]	H, H	4	1.2	82	
17[f]	H, Me	7	193.5	1.57	
		0.7	1.88		
17[e]	Me, Me	4	1.2	50	
17[e]	^{i}Pr, ^{t}Bu	5	n.d.	n.d.	
17[f]	^{t}Bu, Me	518	101.3	1.57	222
17[f]	^{t}Bu, ^{t}Bu	1543	265.4	2	223
17[f]	^{t}Bu, OMe	3	91	1.66	222
			1	1.76	
17[e]	CMe_2Ph, Me	175	70	1.9	225
17[f, g]	CMe_2Ph, CMe_2Ph	682	31.4	2.36	223
18[f]	^{t}Bu, Me	0.7	2.89	268	
18[f]	^{t}Bu, ^{t}Bu	3	n.d.	n.d.	264

[a] Cited from Ref [69], [styrene] = 3.5 mol/L (10 mL), toluene 15 ML

[b] Activity in kg-PS/[mol-Ti][styrene mol/L][h]

[c] Determined by GPC. n.d. = not determined

[d] Determined by DSC thermograms

[e] Conditions: Ti 10 μmol, [Al]/[Ti] = 500, 50 °C, 1 h

[f] Conditions: Ti 2.5 μmol, [Al]:[Ti] = 1500, 40 °C, 2 h

[g] Reaction time: 1 h

weight linear polyethylene with uniform molecular weight distribution [72–74], and (ii) high molecular weight amorphous polymers applied to syntheses of ethylene/propylene/diene copolymers (called EPDM, synthetic rubbers) [75–77], ethylene/cyclic olefin copolymers (COC). Moreover, (iii) the catalyst system [V(acac)$_3$ (acac = acetylacetonato)—Et_2AlCl] polymerizes propylene to give not only a syndiotactic "living" polymer with narrow molecular weight distribution (M_w/M_n = 1.05–1.20) [78–80], but also diblock copolymers of propylene and methyl methacrylate (MMA) [78–80]. On the basis of ESR and titration results, vanadium(III) species were postulated to play an important role as the catalytically active species [81–84], although it was estimated that fewer than 1 % of vanadium species were catalytically active in the mixture [83].

One of the main disadvantages of using this type of vanadium catalysts is the deactivation associated with the reduction to inactive vanadium(II) species. Although very high initial activities were observed by adopting these catalysts, the reduction causes very poor overall productivities. This problem could be overcome by reactivation of inactive vanadium(II) center to active vanadium(III) species by addition of re-oxidants such as hexachlorocyclopentadiene [85], ethyl trichloroacetate [86], and the polymerization proceeded without significant decrease in the activity by continuous addition of an aluminum alkyl and the re-oxidants even at high temperature (>105 °C) [86].

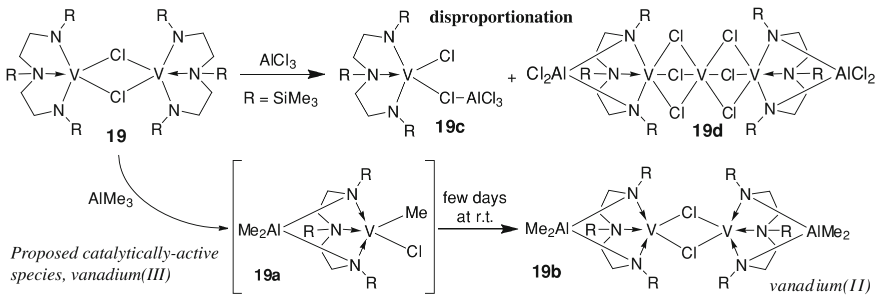
As described above, the classical Ziegler type vanadium catalysts displayed unique characteristics as the olefin polymerization catalysts. Therefore, design and synthesis of new vanadium complex catalysts directed toward the controlled polymerization has been recognized as an attractive target [11–13, 29, 87–90]. Although examples for synthesis of vanadium complexes used as the catalyst precursors for olefin polymerization were known, however, known examples which exhibit the above described unique characteristics of using these transition metal complexes had been limited until recently [20–24, 86, 87–90].

3.2.2.1 Vanadium(III), (IV) Complexes

Vanadium(III), (IV) complexes have been focused on design of the efficient polymerization catalysts, because these were assumed to play an important role as the active species in olefin polymerization. Since only a trace of *actual* active species were present due to that these species would be unstable and be readily reduced by Al cocatalyst to afford the catalytically inactive vanadium(II) species, many researchers thus concentrate on stabilization of the oxidation state of the catalytically active species by an appropriate ligand modification [23, 86].

Dinuclear vanadium(III) chloride complex (**19**) containing bis(amido)amine ligand of type, $(Me_3SiNCH_2CH_2)_2NSiMe_3$, exhibited remarkable catalytic activity for ethylene polymerization in the presence of MAO, Me_2AlCl at 50 °C [activity: 237 kg-PE/mol-V·h (MAO), 660 kg-PE/mol-V·h (Me_2AlCl); ethylene 300 psig (20.4 atm), Al/V = 60 (molar ratio)] [91]. Resultant polyethylene prepared by **19**—Me_2AlCl catalyst possessed high molecular weight with uniform molecular weight distribution ($M_w = 7.21 \times 10^5$, $M_w/M_n = 2.3$). The catalyst system was short-lived, does not remain to be active for no more than 20–30 min, and this may be attributed to the reduction of the vanadium(III) center to an inactive divalent species. The reaction of **19** with $AlMe_3$, Me_2AlCl and MAO in *n*-hexane initially gave a red solution, which after a few days afforded another vanadium(II) complex identified as **19b** (Scheme 3.9). This result thus suggested that no ligand dissociation occurred in the present catalyst system but aggregation with the cocatalyst. The question of how the reduction of **19** afforded the inactive divalent species (**19b**) was thus considered. The reaction of **19** with $AlCl_3$ afforded disproportionated compounds, (tetravalent) **19c** and (one divalent and two trivalent) **19d**, clearly indicating that disproportionation was the basis of a reduction of the vanadium center. These results suggested a possibility of the reduction of **19** affording **19b** and that the addition intermediate **19a**, which is likely to be the catalytically-active species, has the intrinsic instability of a vanadium-carbon bond [91].

A mixed-valent vanadium complex containing dithiolate ligand (**20c**, Scheme 3.10) showed moderate catalytic activity for ethylene polymerization in the presence of both Et_2AlCl and $MgCl_2$ [activity 254 kg-PE/mol-V·h, ethylene 6 atm, 50 °C, 15 min.] [92], but the activity was lower than those by the aryloxo analogues (**20a**, 1990 kg-PE/mol-V·h; **20b**, 1020 kg-PE/mol-V·h), under the same conditions (in *n*-hexane) [92]. The ligand in **20c** transferred to Al alkyls upon treatment with

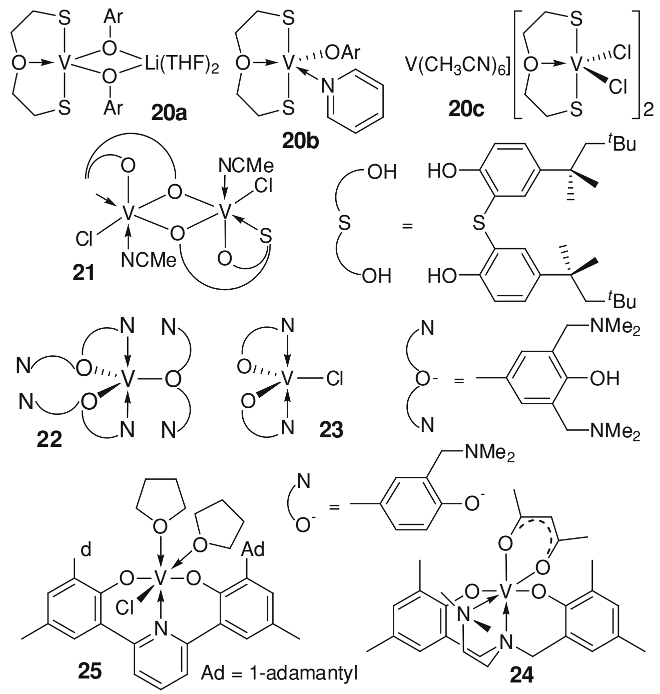


Scheme 3.9 Reaction of dinuclear vanadium(III) chloride complex containing bis(amido)amine ligand [91]

$AlMe_3$ affording vanadium(II) chloride and $[AlMe\{\mu_2\text{-}O(CH_2CH_2S)\}]_2$ [93]. Use of thiobis(phenoxy) ligand improved the activity, and the complex **21** showed remarkable activities in the presence of cocatalyst [activity = 11708 kg-PE/mol-V·h (Al^iBu_3), 8184 (Et_2AlCl), 4736 (MAO); ethylene 5 atm, $Al/MgCl_2/V$ = 100/10/1 (Al^iBu_3, Et_2AlCl) or 3000/10/1 (MAO)] [94]. The resultant polymers possessed unimodal molecular weight distributions ($M_w/M_n = 2.28\text{–}3.12$), suggesting that these polymerizations proceeded with uniform catalytically active species.

Vanadium(III) complexes containing two or three *O*,*N*-chelating aminophenolate ligand (**22**,**23**) exhibited activities for ethylene/propylene copolymerization in the presence of $Et_2AlCl{\cdot}EtAlCl_2$ [95]. The bis(phenoxy) complex (**23**) showed higher activity [159 kg-polymer/mol-V·h·bar, 8 bar of ethylene/propylene (ratio 1/2) in pentamethylheptane at 30 °C for 10 min.] than the tris(phenoxy) complex (**22**, 27 kg-polymer/mol-V·h·bar). Olefin polymerization using a series of vanadium complexes containing an amine bis(phenolate) ligand, $[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(Me_2NCH_2CH_2)N]^{2-}$ (exemplified as complex **24**), with various oxidation states (II-V) were explored [96, 97]. Complex **24** showed notable activity in ethylene polymerization in the presence of $EtAlCl_2$, but showed negligible activity in the presence of MAO [96]. Copolymerizations of ethylene with 1-hexene, norbornene were attempted, but the activities decreased and the resultant polymers possessed a mixture of coplymers with different compositions estimated by their DSC thermograms [96]. Vanadium(III) complex containing bis(phenoxy)pyridine ligand (**25**) showed remarkable catalytic activity for propylene polymerization in the presence of MAO (activity 803 kg-PP/mol-V·h, propylene 5 atm in toluene at 0 °C for 30 min, Al/V = 3000), affording high molecular weight polymer with uniform molecular weight distribution ($M_w = 1.17 \times 10^6$, $M_w/M_n = 2.03$) [98]. The resultant polymer possessed large extent of regio irregular as generally seen in those prepared by vanadium catalysts.

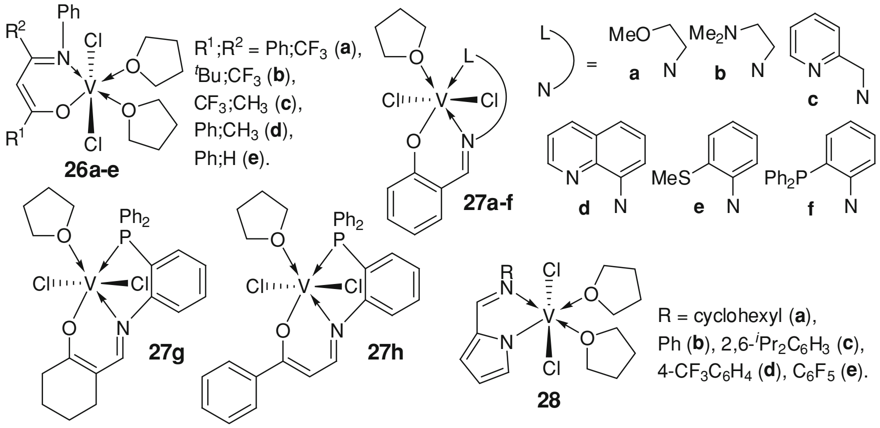
Taking into account the above reports (vanadium complexes using chelate anionic and neutral donor ligands) [91–98], as described above, control, stabilization of the oxidation state, catalytically active species) by an appropriate ligand modification seems to be a key for the efficient catalyst with vanadium(III),



Scheme 3.10 Selected vanadium complexes for olefin polymerization [91–98]

although the *actual* active species including the activation/polymerization mechanism are still not clear at the present stage.

A series of vanadium(III) complexes containing β-enaminoketonato [99, 100], phenoxy-imine [101–104], imino-pyrrolide [105] ligands (exemplified in Scheme 3.11) were tested as olefin polymerization catalyst in the presence of Et_2AlCl and Cl_3CCO_2Et. The selected results are summarized in Table 3.5 [99, 100, 103, 105]. The observed activities by certain complexes were slightly/apparently higher than those by $VCl_3(THF)_3$, and the activities decreased at 70 °C probably due to the rapid deactivation even for short period (5 min) and in the presence of excess amount of re-oxidant (300 equivalent to V). On the basis of these data, it seems that **26b** (R^1;R^2 = ^{t}Bu;CF_3) [99, 100], **26d** (R^1;R^2 = Ph;CH_3) [99, 100], **27 h** [103] showed higher activities. The related phenoxy-imine analogues showed low activities under the same conditions [101–104]. Placement of neutral donor ligands (amine, pyridine) into the phenoxy-imine ligands in **27** was not effective; the observed activity by **27 h** was relatively close to **26e**. Although both the activities and the polymerization behavior were affected by the ligand substituents, the detailed explanation by electronic/steric factors seems difficult (factors such as ligand transfer to Al, reductions etc.). In contrast, the imino-pyrrolide analogues (**28**) showed remarkable activities [105], and the activities by **28** increased in the order (ethylene 1 atm, 50 °C for 5 min): **28c** (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) > **28b**, **e** (Ph, C_6F_5) > **28d**



Scheme 3.11 Selected vanadium(III) complexes as catalyst precursors for olefin polymerization [99, 100, 103, 105]

Table 3.5 Ethylene polymerization by **26–28**—Et_2AlCl—Cl_3CCO_2Et catalyst systems[a]

Complex	Temp. /°C	Activity /kg-PE/mol-V·h	$M_w^b \times 10^{-4}$	M_w/M_n^b
$VCl_3(THF)_3$	25	25800	22.7	2.8
$VCl_3(THF)_3$	50	23400	13.4	5.8
$VCl_3(THF)_3$	70	12600	9.9	21.9
26a	50	27400	17.7	2.6
26b	50	29000	18.6	3.0
26c	50	21800	25.9	2.9
26d	50	24000	17.3	2.9
26e	50	18700	27.1	2.9
27a	50	3840	4.0	2.4
27b	50	9600	3.5	3.0
27c	50	15600	6.2	2.2
27d	50	9120	4.8	2.5
27e	50	7920	6.3	2.0
27f	50	11300	4.6	2.5
27g	50	9360	3.0	2.2
27h	50	20600	2.4	2.0
28a	50	28200	3.5	2.1
28b	50	37800	4.3	2.2
28c	25	39600	6.3	2.4
28c	50	48600	2.5	1.7
28c	70	34200	1.0	2.2
28d	50	33000	4.4	2.4
28e	50	39000	3.0	1.9

[a] Cited from Refs. [99, 100, 103, 105], Reaction conditions: vanadium 0.2 or 0.5 μmol, Et_2AlCl and Cl_3CCO_2Et (ETA), Al/ETA/V = 4000/300/1 (molar ratio), ethylene 1 atm for 5 min

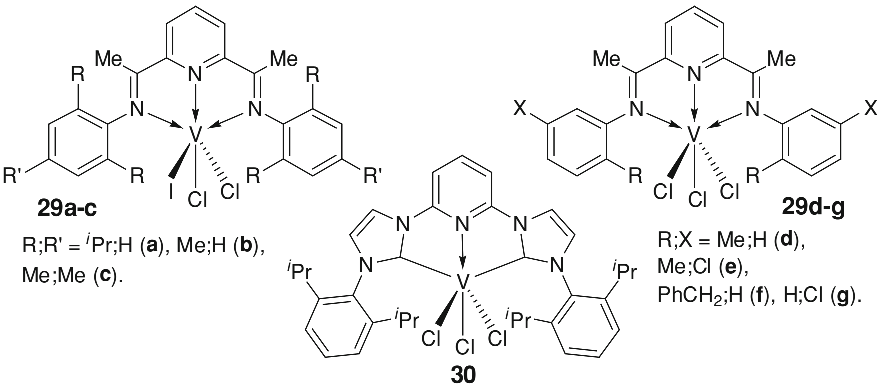
[b] GPC data in 1,2,4-trichlorobenzene versus polystyrene standards

($4\text{-}CF_3C_6H_4$) > **28a** (cyclohexyl). The results thus suggest that both electronic and steric factors play an important role (probably for strong coordination).

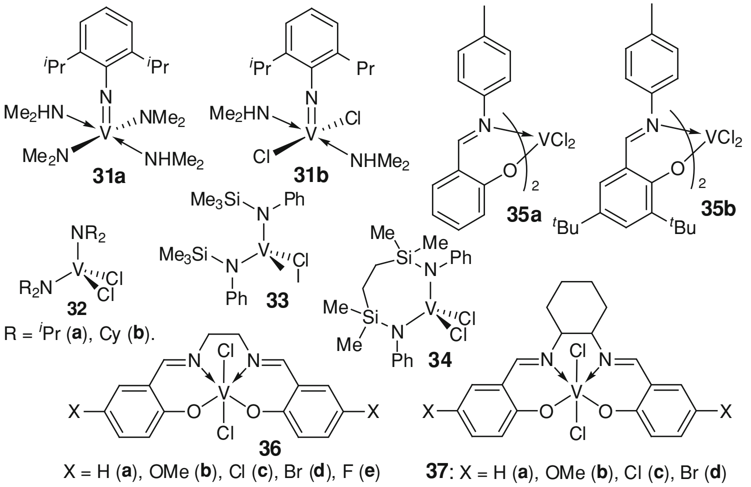
Complex **27c** showed high activity in the ethylene/norbornene copolymerization and the activity was close to that by **27h** under the same conditions, although the activity by **27c** was lower than that by **27h** in the ethylene polymerization [103]. Complexes **28** showed moderate comonomer incorporation with higher activities in ethylene/10-undecen-1-ol copolymerizations, affording the copolymers with relatively low molecular weights ($M_n = 3.1\text{–}52.5 \times 10^3$) [105]: the M_n values decreased upon increasing the comonomer content [105].

Vanadium(III) complex containing neutral bis(imino)pyridine ligand (**29a**) exhibited remarkable catalytic activities for ethylene polymerization in the presence of MAO, affording the polymers with broad molecular weight distributions [activities 1420, 2240 kg-PE/mol-Vh, with Al/V = 600, 60 (molar ratio), respectively; ethylene 100 psig (6.8 atm), 50 °C, 15 or 30 min] (Scheme 3.12) [106]. The activities decreased at 140 °C, and the molecular weight distributions in the resultant polymers were dependent upon the Al/V molar ratios. The reaction with ethylene using the complexes (**29d**, **e**) containing mono substituted aromatic group on the imino ligand (in place of 2,6-diisopropylphenyl) afforded oligomeric mixtures and polyethylene (products by Schultz-Flory distribution) [107], (Dimerization of propylene (selectivity 80–95 %) [108]), and the reaction with propylene by **29f**, **g** afforded oligomers with relatively high C_6 selectivity (80–95 %, major products: methylpentenes) [107], (Dimerization of propylene (selectivity 80–95 %) [108]). These results suggested that the observed trend concerning the ligand effect was very similar to that observed in the ethylene polymerization/oligomerization using iron(II) complexes containing similar ligands [109–115]. The bis(carbene)pyridine complex (**30**) showed remarkable activities for ethylene polymerization, and the activity was affected by the Al cocatalyst employed [116]. The activity decreased in the order (ethylene 1 atm in toluene at r.t. for 30 min, Al/V = 500, molar ratio): 1446 kg-PE/mol-V·h (MMAO, methyl-isobutyl-aluminoxane) > 1280 (MAO) > 586 (dried MAO and Al^iBu_3) > 278 (Et_2AlCl).[59]

(Arylimido)vanadium(IV) dichloride complexes (**31**, Scheme 3.13) showed high activities for ethylene polymerization in the presence of Al cocatalyst [activity by **31b**: 59 kg-PE-mol-V·h (MAO, Al/V = 500), 120 kg-PE-mol-V·h (Et_2AlCl, Al/V = 10); ethylene 1 atm, 20 °C in toluene, 2 or 10 min], affording the polymers with uniform molecular weight distributions [117, 118]. The activities in ethylene/propylene copolymerization using vanadium(IV) complexes containing two amide ligands (**32**) were affected by the Al cocatalyst employed, and the activity by **32a** decreased in the order: $Et_2AlCl{\cdot}EtAlCl_2$ (860 kg-polymer/mol-V·h) > $EtAlCl_2$ (330) > Et_2AlCl (80) > $AlEt_3$ (24) [conditions: ethylene + propylene total 2 bar in hexane at 22 °C for 15 min, Al/V = 40 (molar ratio)] [119]. The isopropyl amide complex (**32a**) showed higher activity than the cyclohexyl analogue (**32b**) [119], and the resultant polymer possessed high molecular weight with uniform molecular weight distribution (**32a**—$Et_2AlCl{\cdot}EtAlCl_2$ catalyst, $M_w = 2.29 \times 10^6$, $M_w/M_n = 3.0$, ethylene 73 wt%). Vanadium(IV) complex with chelate bis(amide)



Scheme 3.12 Vanadium(III) complexes with neutral tridentate donor ligands [106–116]



Scheme 3.13 Selected vanadium(IV) complexes as catalyst precursors for olefin polymerization [117–123]

ligand (**34**) showed higher activity than the bis(amide) analogue (**33**) in ethylene polymerization [activities in the presence of $Et_2AlCl \cdot EtAlCl_2$: 213 kg-PE/mol-V·h, 54 kg-PE/mol-V·h for **34**, **33**, respectively: ethylene 1 atm in toluene at 30 °C, Al/V = 50]. Although the activity in the ethylene polymerization by **36** is close to that by **32a** (178 kg-PE/mol-V·h), **34** showed higher activity in ethylene/propylene copolymerization [120].

Vanadium(IV) complex with N,O-bidentate ligand (**35b**) showed higher activity than **35a**, probably owing to increasing the steric bulk, and the activity was highly affected by the Al cocatalyst employed [$EtAlCl_2 \gg Et_2AlCl > MAO$]. The resultant polymers possessed rather high molecular weights with moderate distributions

[121]. The salen-type tetradentate complexes (**36**, **37**) also showed from moderate to high activities for ethylene polymerization [122, 123], and the activities of **37** were higher than **36**: the activities were affected by the *ortho*- substituent in the phenoxo moiety, and by Al cocatalyst employed. However, the resultant polymer possessed broad molecular weight distributions ($M_w/M_n = 7.3–10.4$), suggesting generation of multiple catalytically active species [122, 123].

3.2.2.2 Vanadium(V) Complexes

As described above, $VOCl_3$ showed moderate activities for ethylene/propylene (co)polymerization in the presence of Al alkyls, however, one of the major concerns associated with use of vanadium(V) complexes as catalysts for Ziegler-Natta polymerizations is a facile reduction to yield lower-valent complexes. Use of arylimido analogues seemed to be promising, because a series of trichloride analogues, $V(NAr)Cl_3$, can be prepared in high yields by treating $VOCl_3$ with various isocyanates (ArNCO) [124–126], and these complexes showed moderate thermal stability, as demonstrated by synthesis of $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(CH_2Ph)_3$ from the trichloride analogues by treating with $PhCH_2MgCl$ in *n*-hexane [127]. The reported fact is noteworthy, because the most common problem encountered in attempts to synthesize vanadium(V) alkyls was the reduction of the metal center upon alkylation. Placement of appropriate alkyl substituent in the arylimido ligand is important for stabilization of the oxidation state upon the alkylation, and the approach is useful for synthesis various vanadium(V)-alkyls [128–131].

It turned out that the arylimido-aryloxo analogue (**38**) showed remarkable activities not only for ethylene polymerization [132–135], but also for ethylene/norbornene copolymerization [136] especially in the presence of halogenated Al alkyls (Et_2AlCl, Me_2AlCl, $EtAlCl_2$ etc.) [134–136], affording high molecular weight polymers with uniform distributions. Selected results in the ethylene polymerization catalyzed by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**38**) are summarized in Table 3.6 [135]. The activity was highly dependent upon the Al cocatalyst employed, and the activities in toluene decreased in the order: ${}^iBu_2AlCl$ (52000 kg-PE/mol-V·h) > $EtAlCl_2$ (37400) > Me_2AlCl (27500) > Et_2AlCl (11700) > MAO (2930) $\gg$ $Et_2Al(OEt)$, Me_3Al, Et_3Al (trace or less). The activity did not decrease after 30 min, and was highly affected by the solvent employed; the activity of 584000 kg-PE/mol-V·h (TOF 20800000 h^{-1}, 5780 s^{-1}) was attained in CH_2Cl_2 in the presence of $EtAlCl_2$. The resultant polymers prepared in toluene possessed ultra high molecular weights with unimodal molecular weight distributions (the M_v values in the resultant polymers prepared in the presence of ${}^iBu_2AlCl$, Me_2AlCl were $9.87–12.5 \times 10^6$, 8.98×10^6, respectively). The activity decreased upon addition of CCl_3CO_2Et, which is commonly used as the effective additives in the polymerization using vanadium(III) and/or vanadium(IV) complexes. The results clearly suggest that the active species were thus different from those prepared from vanadium(III), (IV) complexes. It was assumed that the observed difference in the catalytic activities in the presence of MAO and Et_2AlCl

Table 3.6 Ethylene polymerization catalyzed by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**38**)—Al cocatalyst systems: effect of Al cocatalyst[a]

38 / μmol	Al cocat.	Time / min	Activity[b] × 10^{-3}	TOF[c] × 10^{-5}	$M_w^d \times 10^{-5}$	M_w/M_n^d	$M_v^e \times 10^{-6}$
1.0	MAO	10	2.93	1.04	28.7	1.64	
0.05	Me_2AlCl	10	27.5	9.8	–[e]	–	8.98
0.05	Et_2AlCl	10	11.7	4.15	36.5	1.42	
0.05	Et_2AlCl	30	11.4	4.06			
0.05[f]	Et_2AlCl	10	1.08	0.4			
0.05	$^iBu_2AlCl$	10	52.0	18.5	–[e]	–	9.87
0.01	$^iBu_2AlCl$	10	64.8	23.1	–[e]	–	12.5
0.05	$EtAlCl_2$	10	37.4	13.3	6.02	3.04	
1.0	Et_2AlOEt	10	None	–			
1.0	Me_3Al	10	Trace	–			
1.0	Et_3Al	10	Trace	–			
1.0	$^iBu_3Al$	10	trace	–			

[a] Data cited from Ref. 135, reaction conditions: toluene + cocatalyst solution = 30 mL, 0 °C (or 25 °C by MAO), ethylene 8 atm, Al cocatalyst 250 or 500 μmol (or MAO 2.5 mmol)

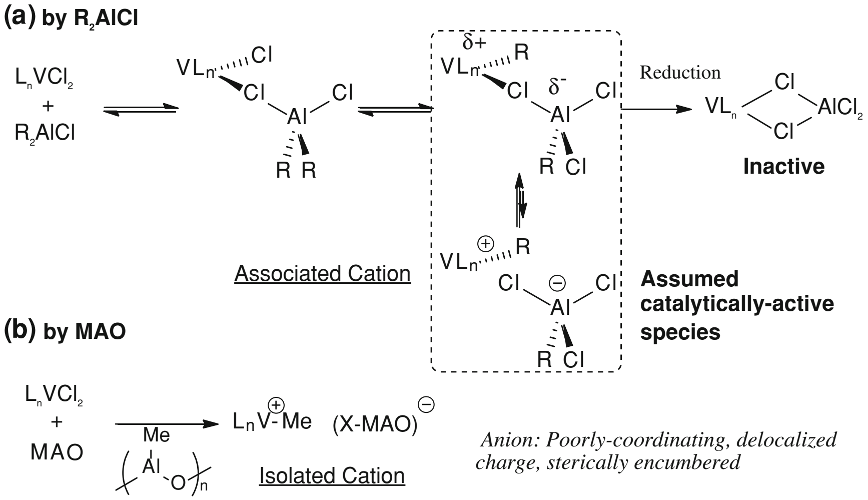
[b] Activity in kg-polymer/mol-V·h

[c] TOF = (molar amount of ethylene consumed)/(mol-V·h)

[d] GPC data in o-dichlorobenzene versus polystyrene standards

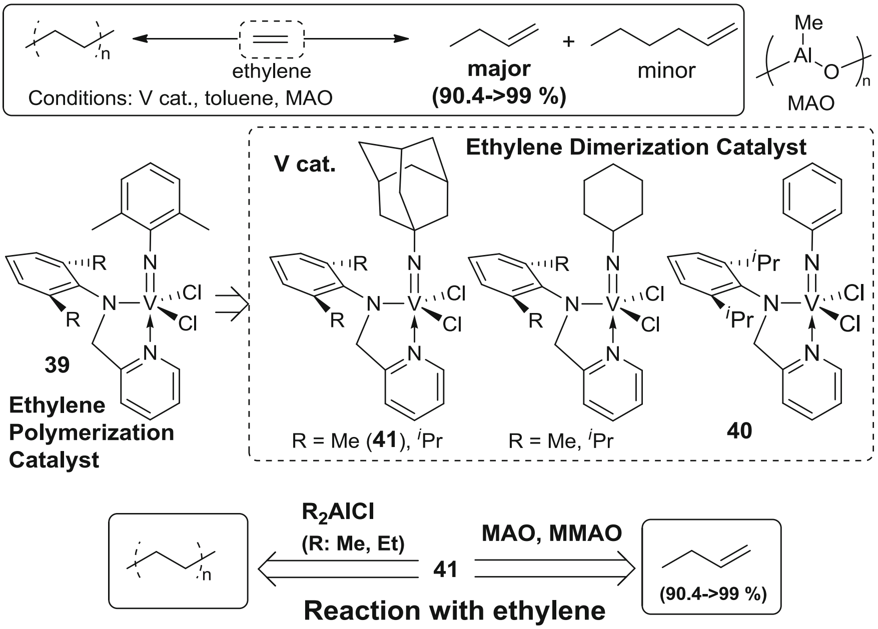
[e] Molecular weight by viscosity due to that the resultant polymers were insoluble in *o*-dichlorobenzene for GPC measurement

[f] Polymerization in the co-presence of $CC_{13}CO_2Et$ (10.0 equiv to V)



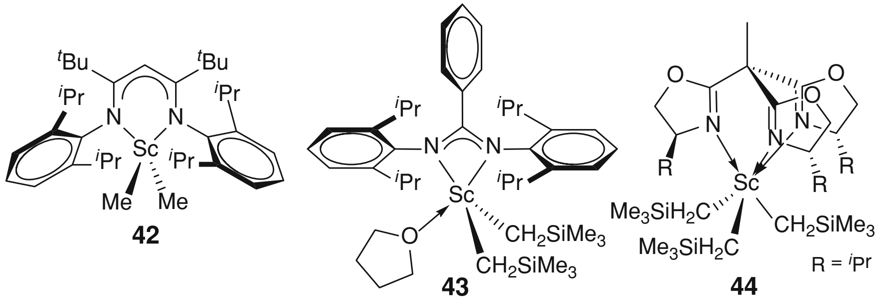
Scheme 3.14 Proposed formation of two catalytically active species [23, 134, 135, 140]

cocatalyst would be due to the different catalytically active species, catalyst/cocatalyst nuclearity effect [137, 138] generated in the two catalyst systems, as shown in Scheme 3.14 [23].



Scheme 3.15 Ethylene dimerization by (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand [139, 140]

The (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand, $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ [R = 1-adamantyl (Ad), cyclohexyl (Cy), phenyl (Ph)], exhibited remarkably high catalytic activities for ethylene dimerization in the presence of MAO, affording 1-butene exclusively (selectivity from 90.4 to $>$ 99 %, Scheme 3.17) [139]. The phenylimido analogue (**40**) also afforded 1-butene under the same conditions, whereas the 2,6-dimethylphenylimido analogue (**39**) afforded polyethylene. The cyclohexylimido analogues also showed high activities to afford 1-butene exclusively. The adamantylimido analogues (**41**) showed the highest activities (TOF: 2730000 h^{-1}) for ethylene dimerization. These results thus clearly indicate that (i) the electronic nature of the imido ligand directly affects the activity, and (ii) the steric bulk of the imido substituents plays an essential key role toward the selectivity in this catalysis [139]. Moreover, **41**—Et_2AlCl, Me_2AlCl afforded ultra high molecular weight polyethylene, suggesting a presence of proposed reaction scheme shown in Scheme 3.15 [140]. On the basis of reactions under various conditions, and ESR and NMR experiments, it was thus proposed that cationic vanadium(V)-alkyls play an important role in these catalysis [140].

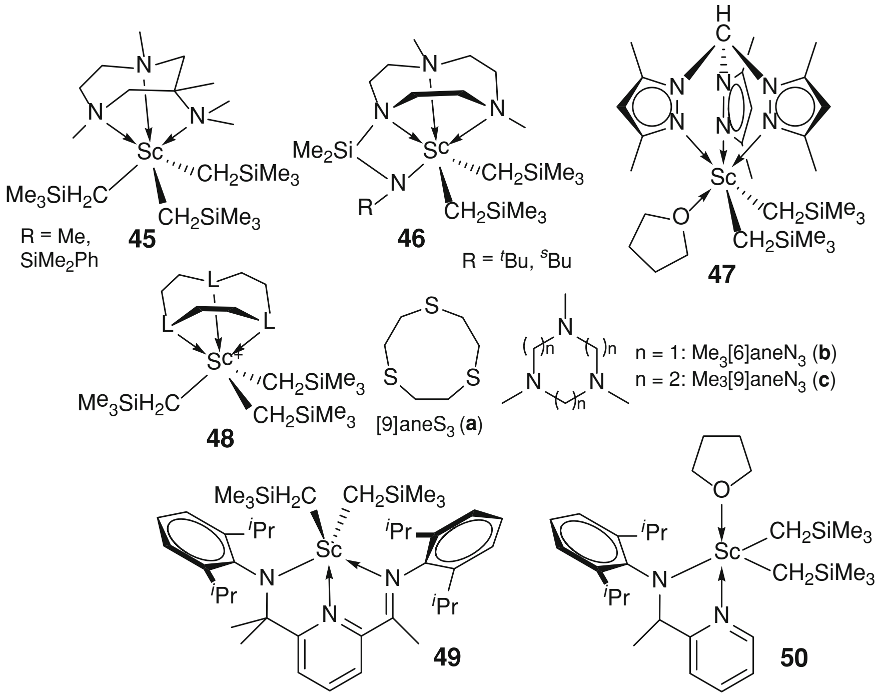


Scheme 3.16 Known scandium catalysts for olefin polymerization [141–143]

3.2.3 Miscellaneous Early Transition Metal Complex Catalysts

3.2.3.1 Scandium Complexes

Examples for olefin polymerization using non-metallocene type scandium complex catalysts still have been limited but demonstrate promising possibilities: examples as catalyst precursors for conjugated diene polymerization (butadiene, isoprene) have also been reported. The complex containing β-diketiminato "nacnac" (**42**, Scheme 3.16) exhibited moderate to high catalytic activities for ethylene polymerization [1200 kg-PE/mol-Sc·h (MAO, Al/Sc = 20), 300 kg-PE/mol-Sc·h {$B(C_6F_5)_3$, ca. 1 equiv.}: ethylene 300 psi, 50 °C, cyclohexane/toluene], affording high molecular weight polymers with uniform distributions ($M_w = 8.51\text{–}18.7 \times 10^5$, $M_w/M_n = 1.7\text{–}2.48$) [141]. The reaction of **42** with 1.0 equiv. of $B(C_6F_5)_3$ afforded monocationic $[(\text{nacnac})\text{ScMe}]^+[\mu\text{-Me-B}(C_6F_5)_3]^-$, and the dicationic species $[(\text{nacnac})\text{Sc}]^{2+}[\mu\text{-Me-B}^-(C_6F_5)_3]_2$ by treating **42** with 2.0 equiv. of $B(C_6F_5)_3$ exhibited moderate catalytic activity for ethylene polymerization (1 atm at r.t.) [141]. In contrast, ethylene polymerization using the admidinate analogue, $[\text{ArNC(Ph)NAr}]\text{Sc}(CH_2SiMe_3)_2(\text{THF})$ (**43**) was low [activity 120 kg-PE/mol-Sc·h, ethylene 5 bar, $\{PhN(H)Me_2\}(C_6F_5)_4$, 30 °C 20 min], and the acitivity by the Y, Gd, Nd complexes showed higher catalytic activities ($1.0\text{–}1.5 \times 10^4$ kg-PE/mol-M·h) under the same conditions [142]. A dicationic scandium complexes containing a C_3-chiral ligand, prepared from $[^i\text{Pr-trisox}]\text{Sc}(CH_2SiMe_3)_3$ (**44**) with 2.0 equiv. of $[Ph_3C][B(C_6F_5)_4]$, exhibited remarkable catalytic activities for 1-hexene polymerization [$2.03\text{–}36.2 \times 10^3$ kg-polymer/mol-Sc·h at −30–21 °C], and the activity increased at higher temperature. The resultant polymer prepared at −30 °C possessed highly isotactic structure (*mmmm* = 90 %) with narrow molecular weight distribution ($M_w/M_n = 1.18$, $M_w = 7.50 \times 10^5$), suggesting a possibility of living polymerization [143]. In addition to promising results by half-metallocene type scandium complex in ethylene copolymerization (with styrene, cyclic olefins etc.) [144–147], these results suggest that the non-metallocene type scandium complexes



Scheme 3.17 Reported scandium dialkyl, trialkyl analogues [148–153]

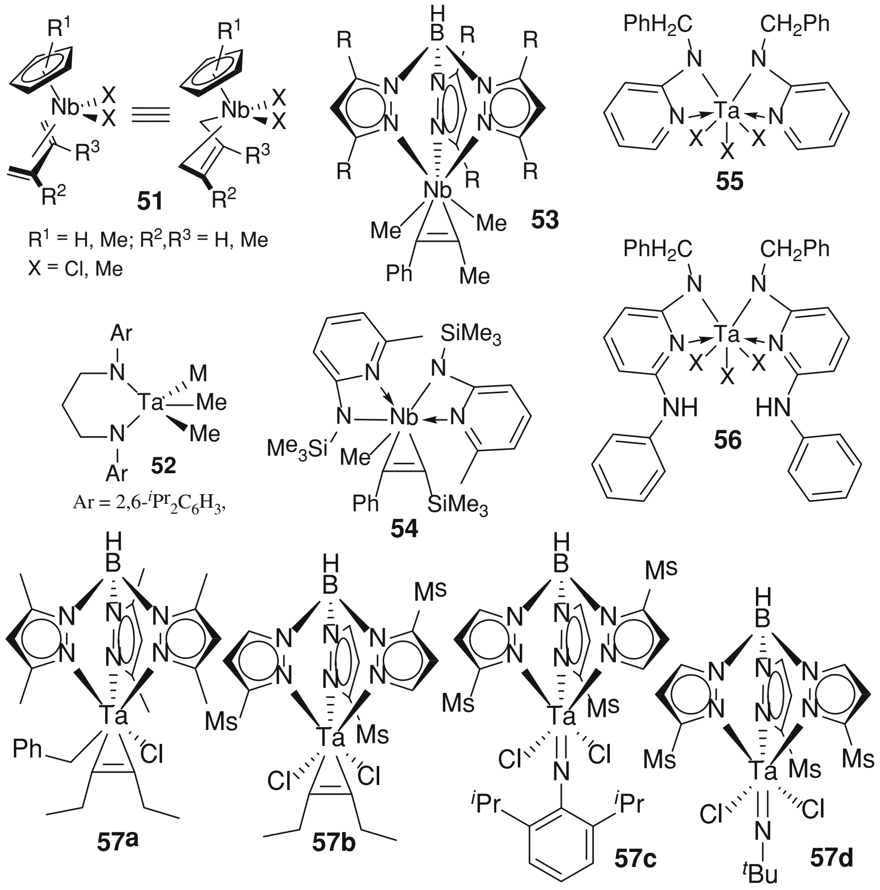
would exhibit unique characteristics as the catalyst precursors for olefin polymerization.

Scandium complexes containing [6-amino-6-methyl-1,4-diazepine] ligand (**45**, Scheme 3.17) exhibited high activities for ethylene polymerization in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, affording polymer with unimodal molecular weight distribution [2660 kg-PE/mol-Sc·h, ethylene 5 bar, in toluene at 50 °C]: the activity increased at 70 °C (5800 kg-PE/mol-Sc·h) [148]. Although the dialkyl analogues containing monoanionic tridentate ligand, $Sc(L)(CH_2SiMe_3)_2(THF)$ [L = 6-RN-1,4,6-trimethyl-1,4-diazepine] (R = Me, $PhMe_2Si$), exhibited negligible catalytic activities for ethylene polymerization in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, the THF-free complex exhibited high activity under the same conditions [2920 kg-PE/mol-Sc·h, ethylene 5 bar, toluene, 50 °C, 10 min], affording high molecular weight polymer with uniform distribution ($M_w = 1.2 \times 10^6$, $M_w/M_n = 1.9$) [149]. Removal of THF is thus found to be prerequisite for exhibiting remarkable activity. Ethylene polymerization using Sc complexes containing linked triazacyclononane(TACN)-amide ligands, $[Me_2Si(Me_2TACN)(NR)]Sc(CH_2SiMe_3)_2$ (**46**, R = ^{t}Bu, ^{s}Bu), were explored in the presence of borate cocatalysts [150]. These complexes exhibited high catalytic activities at 70 °C in the presence of $[Ph_3C][B(C_6F_5)_4]$ [activity = 2705 kg-PE/mol-Sc·h (R = ^{t}Bu), 1810 kg-PE/mol-Sc·h (R = ^{s}Bu): ethylene 5 bar, toluene, 10 min], affording relatively high molecular weight polymers with uniform distributions. The activity in the presence of $[Ph_3C][B(C_6F_5)_4]$ was higher than that in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, and the activity at 70 °C was higher than that conducted at 50 °C. The yttrium analogues exhibited further higher catalytic activities under the same conditions [150].

Trialkyl complexes containing four different neutral tridentate ligands (**47**, **48a–c**) were used as the catalyst precursors for polymerization of ethylene, 1-hexene in the presence of $[Ph_3C][B(C_6F_5)_4]$ in toluene (ethylene 6 bar, 33–36 °C, 10 min). Ring size of the tridentate ligand affected the activity for ethylene polymerization [activity = 60 kg-PE/mol-Sc·h (**48b**), 4380 kg-PE/mol-Sc·h (**48c**)], and replacement of NMe group with S (**48a**) was also effective (activity = 5160 kg-PE/mol-Sc·h): the $HC(Me_2pz)_3$ analogue (**47**) also exhibited high catalytic activity (4980 kg-PE/mol-Sc·h). However, the resultant polymers possessed broad molecular weight distributions, although the 1-hexene polymerizations resulted in the polymers with uniform molecular weight distributions in most cases [151]. Taking into account these results, design of cationic Sc(III) alkyl complexes play an essential key role as the active species for olefin polymerization, and the ligand modifications which stabilize the oxidation state should be important for the efficient catalyst. Later, monoanionic bidentate or tridentate anilido-pyridine ligands (**49**, **50**) were prepared and their catalyst performances for ethylene polymerizations were explored [152, 153].

3.2.3.2 Niobium and Tantalum Complexes

The Nb complexes **51** can be considered to contain either a neutral butadiene (C_4) ligand and a Nb(III) metal center or a dianionic butadienide (C_4^{2-}) ligand and a Nb(V) center (Scheme 3.18) [154]. The activity in ethylene polymerization by Cp^*NbMe_2(butadiene) was 39 kg-PE/mol-Nb·h, affording high molecular weight polymer with narrow molecular weight distribution. PDI (M_w/M_n) values are very small (1.05) when these polymerizations were performed at low temperature (−20 °C), suggesting the polymerization proceeds in a living manner. Half-metallocene analogue, $Cp^*Ta(=N^tBu)Cl_2$, exhibited high catalytic activity for ethylene/1-octene copolymerization [40200 kg-polymer/mol-Ta·h: ethylene 500 psig (ca. 34 atm), 140 °C, 15 min] in the presence of Al imidazolide ($[HNMe(C_{18}H_{37})_2][(C_6F_5)_3AlNC_3H_3NAl(C_6F_5)_3]$), affording the copolymer with uniform molecular weight distributions [155]. The activity was higher than that by the bis(amide) analogue (**52**, 6000 kg-polymer/mol-Ta·h) [155]. Niobium complexes containing tris(pyrazolyl)borate ligand (**53**) exhibited moderate catalytic activity for ethylene polymerization in the presence of $B(C_6F_5)_3$, and the activity was affected by the R substituent: the methyl analogue (R = Me) exhibited higher activity (130 kg-polymer/mol-Nb·h) than the H analogue. Treatment of the pre-catalyst with MAO does not result in any polymerization [156]. Bis(pyridyl-amido) niobium(V) (**54**) showed activity for ethylene polymerization upon addition of $B(C_6F_5)_3$, but the activity was low (4.4 kg-polymer/mol-Nb·h) and rapid



Scheme 3.18 Reported niobium and tantalum complexes for olefin polymerization [154–159]

decomposition of the catalytically active species was observed [157]. Analogous bis(pyridylamide) complexes (**55**, **56**) showed very high activity, up to 23900 kg-PE/mol-Ta·h (ethylene 5 bar, 80 °C), and rapid decrease in the activity was observed at low temperature [158].

More recently, four Ta complexes bearing tris(pyrazolyl)borate ligands (**57a**–**d**) were found to exhibit catalytic activities for ethylene polymerization. Activity in the presence of $\mathrm{Al}^{i}\mathrm{Bu}_3/[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ is higher than that in the presence of dried MAO; the sterically encumbered **57c**, **d** showed higher activities [activity: 77100 kg-PE/mol-Ta·h (**57c**) and 51300 kg-PE/mmol-Ta·h (**57d**)], and some of the highest values reported to date for Ta-based catalysts [159].

3.3 Summary and Outlook

As described above, tremendous number of reports have been known for this project, and some of them are very important from both academic and industrial point of view [20–28]. It is clear that fine-tuning of the ligand plays a crucial role in this catalysis. Unfortunately, recent examples for chromium complex catalysts are not listed and these are also important on relevance of their ethylene trimerization catalysts [160]. Very successful examples such as highly isospecific polymerization of α-olefins, and living polymerization, so called chain shuttling polymerization have been demonstrated among recent advances in this research subject. These several promising findings that should be very important from both academic and industrial viewpoints have been demonstrated. These efforts will pave new promising possibilities for evolution of new *fine* polyolefins with unique properties by incorporation of new comonomers and/or by adopting new synthetic strategies. We highly expect more progress in this field in the near future.

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Chapter 4
Olefin Polymerization with Non-metallocene Catalysts (Late Transition Metals)

Daisuke Takeuchi

Abstract Diimine Pd and Ni complexes catalyze the polymerization of ethylene, propylene, and α-olefins. The reaction involves isomerization of the growing terminal (chain walking) and, as its result, produces highly branched polyethylene and poy(α-olefin)s having a smaller number of the alkyl substituents than expected from the monomer structure. Ni complexes with salicylaldimine or iminocarboxamide ligands and Pd complexes with phosphinesulfonate ligands are used as single component catalysts for ethylene polymerization. Especially, the latter catalysts show tolerance towards polar functional groups and promote copolymerization of ethylene with wide varieties of polar monomers. The Pd and Ni complexes are able to catalyze ethylene polymerization in aqueous media to yield polyethylene particles. Fe and Co complexes with bis(imino)pyridine ligands show high catalytic activity for ethylene polymerization to yield linear polyethylene. Complexes of the metals such as Rh, Ir, Ru, and Ag were revealed to become catalytically active by proper design of the ligand. Not only monometallic complexes but also bimetallic or multimetallic complexes are used for ethylene polymerization. Late transition metal complexes catalyze selective cyclopolymerization of non-conjugated dienes and trienes to afford the polymers with cycloalkane groups with controlled stereochemistry.

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4.1 Introduction: Brief History of Late Transition Metal Catalysts for Olefin Polymerization

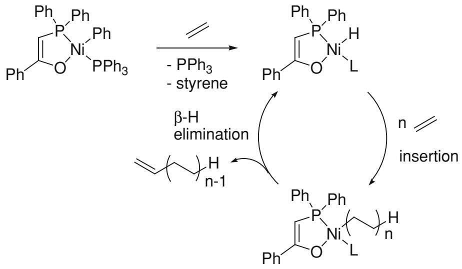
Ziegler-Natta catalysts enabled polymerization of ethylene under low pressure (even atmospheric pressure), synthesis of high density polyethylene, and stereospecific polymerization of propylene [1]. The catalysts composed of early transition metal compounds, especially, of Ti. In fact, the discovery begins with a late transition metal, Ni, during the studies on oligomerization of ethylene by organoaluminums (Aufbaureaktion). Ziegler observed formation of 1-butene in the reaction of ethylene with organoaluminums and found that a trace amount of nickel actually catalyzes the reaction in 1953 [2]. This serendipitous founding motivated him to survey all the available metal salts for the catalysts, and ended up with the discovery of $TiCl_4$ and $AlEt_3$ as the catalyst for ethylene polymerization. Natta expanded the work and discovered in 1954 that the catalyst containing $TiCl_3$ is effective for stereospecific polymerization of propylene [1]. It is also remarkable because of the high utility of isotactic polypropylene for commercial use.

In 1980, Kaminsky found that methylaluminoxane, which is formed by controlled hydrolysis of $AlMe_3$, works as the excellent co-catalyst in combination of metallocene complexes of group 4 metals [3]. The discovery of the metallocene catalysts allows detailed mechanistic studies on the polymerization and accurate design of the catalyst for the controlled polymerization of olefins. The active species of the polymerization is cationic metallocene bonded to the long alkyl group, and coordination of olefin to the electron-deficient metal center followed by migratory insertion of the olefin to metal-carbon leads to the chain growth.

Until recently, the homogeneous catalysts for olefin polymerization had been limited to the complexes of early transition metals. These complex catalysts promote polymerization and copolymerization of olefins in sufficient activity. But such early transition metal complexes, upon activation with the organoaluminum cocatalyst, have high affinity towards water and molecules with polar functional groups, such as esters and amides. Therefore, the polymerization should be conducted in non-polar solvents with exhaustive removal of moisture and air. It has been very difficult to promote copolymerization of hydrocarbon olefins with the olefins with functional groups, such as acrylates.

From that viewpoint, late transition metal complexes had been attractive as a new catalyst for olefin polymerization. As for ethylene oligomerization, Ni catalyst has been reported to show high catalytic activity in 1978 by Keim [4] (Scheme 4.1). This chemical process to form linear α-olefins is called as Shell Higher Olefin Process and is actually commercialized by Shell Co. The oligomerization involves ethylene coordination to the nickel center and its migratory insertion into the Ni–C bond, similar to the olefin polymerization by early transition metal catalysts. The reaction, however, is accompanied by frequent chain transfer reaction via β-hydrogen elimination, and produces oligomer, not polymer, of ethylene.

Scheme 4.1 Mechanism of ethylene oligomerization by SHOP catalyst



In 1995, Brookhart discovered that Ni and Pd complexes with diimine ligands show high catalytic activity for ethylene and olefin polymerization [5]. Characteristic properties of the catalysis were reported, such as formation of branched polymer in ethylene polymerization and copolymerization of ethylene and acrylate. The discovery of Brookhart catalyst is followed by varieties of late transition metal catalysts.

In 1998, Benett [6], Brookhart [7], and Gibson [8] reported that Fe and Co complexes with bis(imino)pyridine catalyze efficient ethylene polymerization to afford linear polyethylene. In 2000, Grubbs reported that neutral Ni complex with salicylaldimine ligand promotes polymerization of ethylene in the absence of cocatalyst [9]. The catalyst is tolerant toward polar functional groups and promotes copolymerization of ethylene with polar monomers. Recently, Pd complexes with phosphinesulfonate ligand, a chelating monoanionic one, were found and have attracted much attention because of the catalytic activity for copolymerization of ethylene with wide varieties of polar monomers [10].

In this chapter, recent progress on late transition metal-catalyzed olefin polymerization for these two decades is summarized [11–19]. Fundamental reaction results, performance of various catalysts, mechanistic aspects and applications to polymerization of new monomers and coplymerizations are also included.

4.2 Polymerization of Olefins Catalyzed by Cationic Pd and Ni Complexes with Neutral Ligands

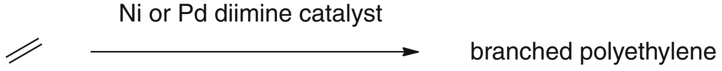
The Ni and Pd complex catalysts for ethylene polymerization can be categorized into two groups: (1) cationic complex with neutral bidentate ligand (Brookhart type) and (2) neutral complexes with monoanionic bidentate ligands (Grubbs type). Although most precursors of the former catalyst are neutral ones with two halogeno or pseudohalogeno ligands, addition of the cocatalysts generates cationic active species for polymerization. Thus, they are classified as the cationic catalysts in this chapter. The latter seems to have its origin in SHOP catalysts for ethylene oligomerization.

4.2.1 Cationic Ni and Pd Catalysts with Diimine Ligands

Square planar Ni(II) and Pd(II) complexes with diimine ligands (Chart 4.1, **1a–1i**) show high catalytic activity for ethylene polymerization [5, 14, 17, 19]. Ortho-substituents on *N*-aryl groups are essential for high catalytic activity and formation of high molecular weight polymer. Diimine Ni complexes are frequently used in combination with organoaluminum cocatalyst, where the cationic diimine Ni-alkyl complex is produced in situ similar to the metallocene catalysts. As for organoaluminum, Et_2AlCl or Me_3Al are usable in addition to MAO or MMAO [17]. Cationic methylpalladium complexes with diimine ligand can be isolated much more easily than the Ni complex. Stoichiometric reaction of neutral (diimine)PdMeCl complexes with NaBARF (BARF = $B\{C_6H_3(CF_3)_2\text{-}3,5\}_4^-$) yields the cationic catalyst precursor. Cationic complexes **1g** with a methyl ligand and **1h** with a chelated methoxycarbonyl propyl ligand are isolated and used as the single component catalyst.

4.2.1.1 Polymerization of Ethylene and α-Olefins

The Ni and Pd complexes promote polymerization of ethylene at room temperature or below, affording high mass polymer (Eq. 4.1). Produced polyethylenes adopt highly branched structure and show their glass transition temperature at −85 to −46 °C. Degree of the branch depends largely on the reaction conditions and catalysts. Generally, Pd catalysts afford polyethylene with higher degree of branches, compared to those obtained by the Ni catalysts.



(4.1)

The formation of branches is ascribed to the isomerization of growing terminal during the polymerization (Scheme 4.2) [20]. (The scheme is presented with a solvated intermediate, but another coordinatively unsaturated species with agostic interaction of β-hydrogen are also observed in the reaction mixtures.) The Ni and Pd species having the growing polyethylene as the alkyl ligand undergo β-hydrogen elimination to afford an olefin-coordinated hydride-metal species. Coordination of ethylene at an apical site of the complex may lead to its exchange with the π-coordinated polymer and subsequent chain transfer. The sterically hindered diimine ligand of the complex does not allow the associative exchange of the coordinated polymer with a monomer, and causes re-insertion of the vinyl group of the polymer into the metal-hydrogen bond. Thus, the polymer growth continues to yield the branched polyethylene with high molecular weight. 1,2-Insertion of the terminal vinyl group of the polyethylene into the M–H bond yields *prim*-alkyl metal species, while 2,1-insertion forms *sec*-alkyl metal species. β-Hydrogen elimination and re-insertion of the vinyl-terminated polyolefin with different regioselectivity

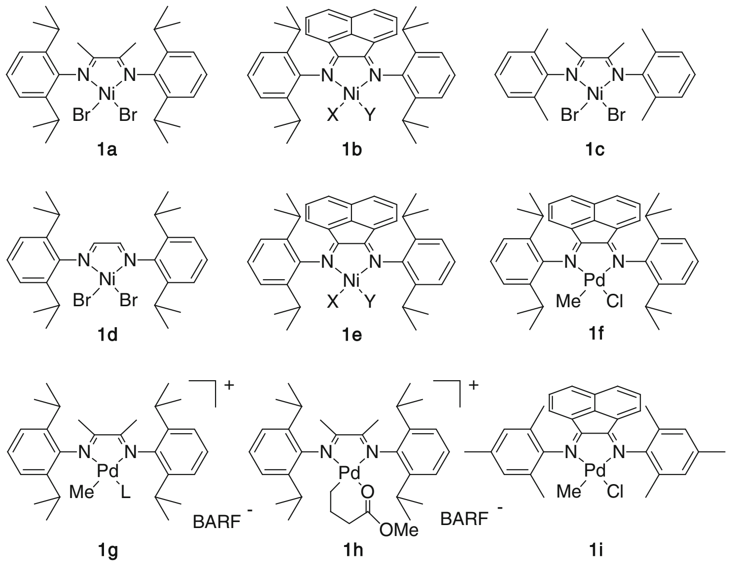
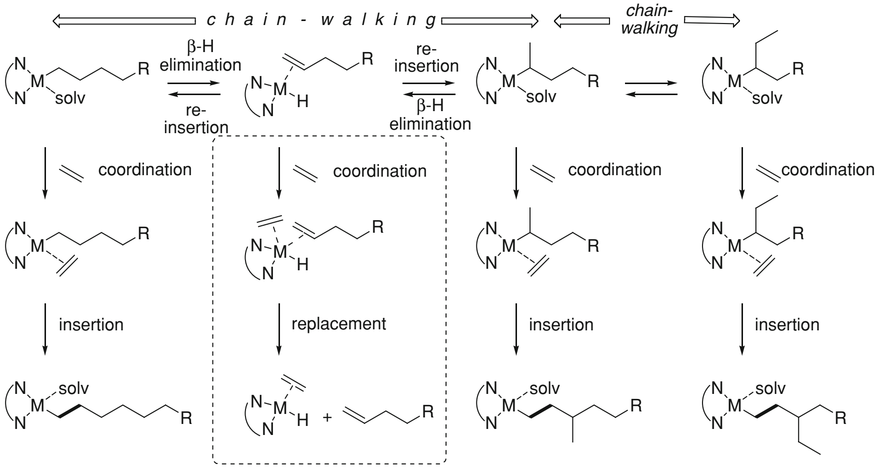
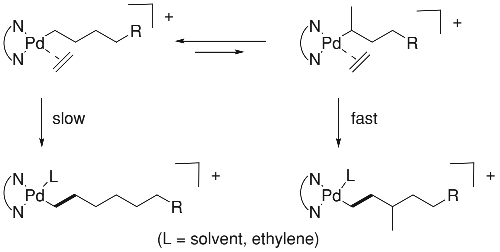


Chart 4.1 Representative diimine Ni and Pd complexes



Scheme 4.2 Mechanism of formation of branches

shift position of the metal attached to the alkyl group to its adjacent carbon. Repetition of this process may occur along the polymer chain, which is named as “chain walking”. Insertion of ethylene to the CH(Me)–M bond or CH(R)–M bond of the *sec*-alkyl metal species results in a branched structure.



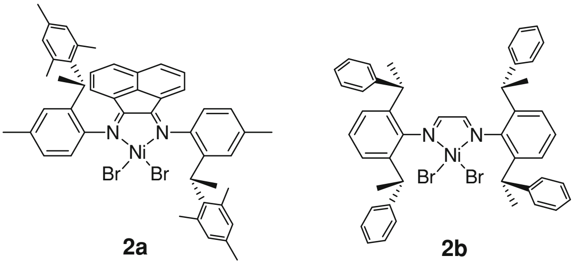
Scheme 4.3 Thermodynamic and kinetic features of ethylene insertion

Further details are shown in Scheme 4.3. Ethylene-coordinated *prim*-alkyl Pd species and *sec*-alkyl Pd species are in equilibrium via chain walking, and both of the complexes allow insertion of the coordinated ethylene to the C–Pd bond [21, 22]. In the absence of ethylene, secondary alkyl species is more favorable, but the equilibrium is shifted toward formation of the primary alkyl Pd species in the presence of ethylene at room temperature. On the other hand, insertion of ethylene takes place more rapidly to *sec*–alkyl–Pd bond compared to that to *prim*–alkyl–Pd bond. Both the chain walking and the insertion of ethylene take place smoothly, which results in formation of the highly branched polyethylene.

The Pd-catalyzed ethylene polymerization under atmospheric pressure produces the polymer with high degree of branching, but the polyethylene obtained from the reaction under high ethylene pressure (over 10 atm) has longer main chain and shorter branches based on results of rheological investigation [23, 24] and theoretical calculation [25].

Living polymerization of ethylene is achieved by the Ni- and Pd-diimine catalysts. For example, Pd complexes **1g** (L = MeCN) and **1h** bring about polymerization of ethylene at 5 °C at 7–27 atm to yield polyethylene with narrow molecular weight distribution ($M_n = 50{,}000$–$60{,}000$, $M_w/M_n = 1.1$). Polyethylene obtained from complex **1h** as the catalyst has a terminal ester group derived from the ligand of the complex. Terminating end can be also functionalized with aldehyde group by using ω-hydroxy-α-olefin as a terminating reagent [26, 27]. By utilizing the living character of the polymerization, poly(ethylene-*block*-α-olefin) [27] and poly(ethylene-*block*-(ethylene-*co*-CO)) [28] were synthesized by the stepwise addition of the monomers. Owing to high tolerance of the Pd complex toward polar functional groups, the catalysis is successfully applied for the copolymerization of ethylene with varieties of the comonomers (See Chap. 6).

Catalytic activity of the Pd- and Ni-diimine complexes is affected by *N*-aryl groups of the ligand [29, 30]. Guan investigated the electronic effect of the aryl groups of the diimine ligands on the Pd-catalyzed ethylene polymerization systematically [31, 32]. Electron-donating group at *para*-position of the aryl group stabilizes the cationic metal center, increases TON and molecular weight of the products in ethylene polymerization, and enhances incorporation of methyl acrylate comonomer in the copolymerization.

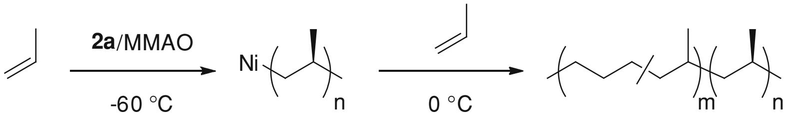


2a **2b**

Chart 4.2 C_2 symmetric Ni diimine complexes

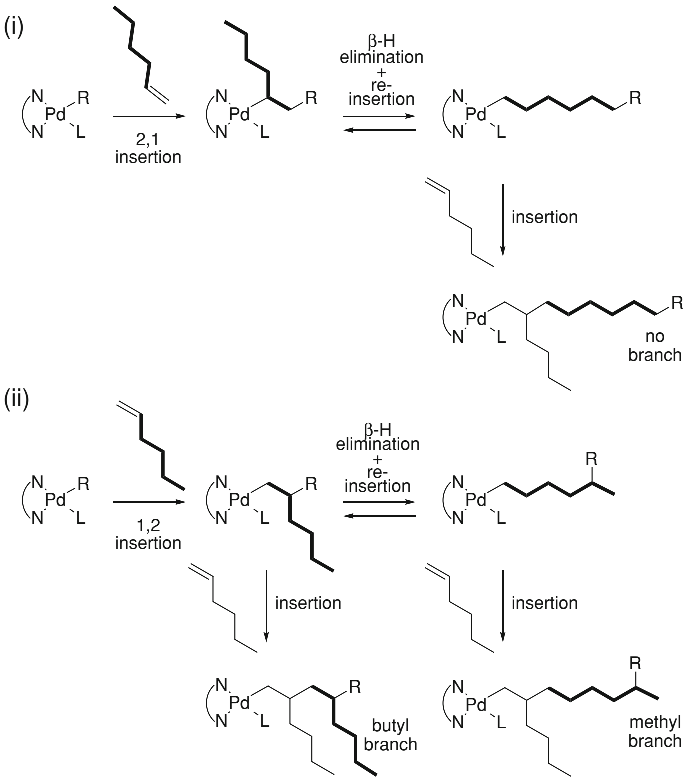
Pd diimine catalysts promote the polymerization of propylene. The structure of the polymer depends on the structure of the catalyst used. ^{13}C NMR of the polymer shows that the polypropylene contains the repeating units with linear structure such as tetramethylene or heptamethylene groups. Isobutyl and 2-methylhexyl terminating group is also observed [33]. Diimine Ni complex **1d** in combination with MAO catalyzes polymerization of propylene below −45 °C to afford polypropylene with a syndiotactic structure ($rr = 74\ \%$) [34]. The above polymerization and that catalyzed by **1b** (X = Me, Y = OEt_2) proceeds via 1,2-insertion of the monomer at the temperature [34, 35]. Insertion in 2,1- and 1,3-regiochemistry also takes place in the polymerization at 0 °C, giving the polymer with lower stereoselectivity (65 %).

Ni complexes with C_2 symmetric ligand (Chart 4.2, **2a**) is effective for living polymerization of propylene at 0 °C to produce the polymer containing both 1,2- and 1,3-repeating units [36]. The polymer formed at −78 °C contains only 1,2-repeating units with isotactic stereochemistry. The isospecific polymerization at −60 °C and further polymerization at 0 °C produces elastomeric polypropylene having crystalline isotactic block and non-crystalline regio-random block (Eq. 4.2) [37, 38].



(4.2)

Propylene polymerization catalyzed by metallocenes proceeds in 1,2-insertion of the monomer. Synthetic organic reactions catalyzed by late transition metal complexes often involve 2,1-insertion of α-olefins into M-H and M–C bond to form *sec*-alkyl group bonded to the metal. Polymerization of α-olefins catalyzed by Ni and Pd complexes has steric difficulty in insertion of a new monomer into the *sec*–alkyl–metal bond formed by the 2,1-insertion. The Ni and Pd complexes with diimine ligand, however, catalyze smooth polymerization of α-olefins [20]. Frequent chain walking of the polymer end results in chain elongation of the monomer to afford the polymer with higher linearity than expected from the monomer structure.



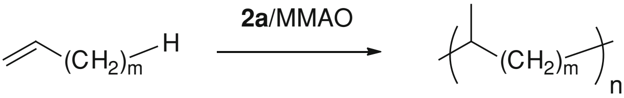
Scheme 4.4 Mechanism of formation of branches in 1-hexene polymerization

Scheme 4.4 summarizes detailed reaction pathways of the polymerization of 1-hexene [20]. In the Pd-catalyzed polymerization of α-olefins higher than 1-pentene, the insertion of the monomer takes place only to CH_2–Pd bond and not to CH(R)–Pd bond. The monomers undergo 1,2- as well as 2,1-insertion to the CH_2–Pd bond during the polymerization. Thus, when 2,1-insertion takes place, the subsequent insertion of another monomer occurs only after the chain-walking reaction, resulting in the repeating unit with linear structure (Scheme 4.4(i)). On the other hand, 1,2-insertion of a monomer to the CH_2–Pd bond yields a new CH_2–Pd bond at the growing polymer end. Next monomer can insert to the CH_2–Pd bond to result in the repeating unit with butyl branch (Scheme 4.4(ii)). The insertion after the chain-walking reaction forms the monomer unit with methyl branch in this case. As its result, only methyl and alkyl branches are observed in the produced polymer.

In contrast, the Ni-catalyzed polymerization of α-olefins produces the polymer containing not only methyl and butyl branches, but also ethyl and propyl branches. This result is accounted for by the insertion of those monomers to CH(R)–Ni bond as well as CH_2–Ni bond.

Ni- and Pd-catalyzed polymerization of 1-hexene proceeds in a living fashion at −10 °C, producing the polymers with narrow molecular weight distribution [39]. Block copolymers of different α-olefins can be synthesized by the subsequent reaction of the two monomers. Pd complex catalyzes block copolymerization of ethylene with 1-octadecene to produce highly branched polyethylene block and poly(1-octadecene) block.

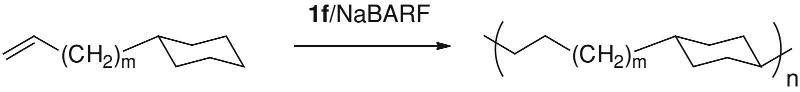
C_2 symmetric Ni diimine complex (**2a**) promotes living polymerization of α-olefins at −40 °C to form the polymer having methyl branches at regulated intervals along the polymer chain (Eq. 4.3).



(4.3)

The polymerization proceeds via selective 1,2-insertion of the monomer followed by chain walking to form the primary alkyl group bonded to the Ni prior to further insertion of a monomer [40]. Tolerance of the Ni- and Pd-diimine complexes toward functional groups enables copolymerization of 1-hexene with silyl vinyl ethers [41] and formation of a hydrocarbon polymer with the terminal acrylamide group [42]. Copolymerization of 1-hexene with olefin having an ureidopyrimidinone group yields the polyolefin which is aggregated by intermolecular cross-linked multiple hydrogen bonding between the functional groups [43]. As the hydrogen bond is cleaved at high temperature, the produced polyolefin shows thermoplastic elastomeric properties.

Alkenylcyclohexanes undergo smooth isomerization polymerization by the Pd-diimine catalysts. The resulted polymers contain only repeating units with 1,4-*trans*-fused six membered ring (Eq. 4.4). The intervals between the six-membered rings are determined by the spacer length between the vinyl and cyclohexyl groups of the monomer. Depending on the density of the cyclohexane group, the melting point of the polymer can be varied from 130 to 220 °C [44].



(4.4)

4.2.1.2 Modified Diimine Ni and Pd Complexes

Modification of the Ni- and Pd-diimine complexes improved the catalytic performance significantly. Rieger prepared the Pd and Ni complexes with 2,6-diarylphenylimino groups at the coordinating nitrogen of the ligand (Chart 4.3, **3a**, **3b**) [45]. Due to the steric repulsion between the bulky aryl substituents, the two *N*-aryl planes are twisted from each other. Remarkably, the Ni complex catalyzes olefin polymerization even in the presence of hydrogen [46], although common

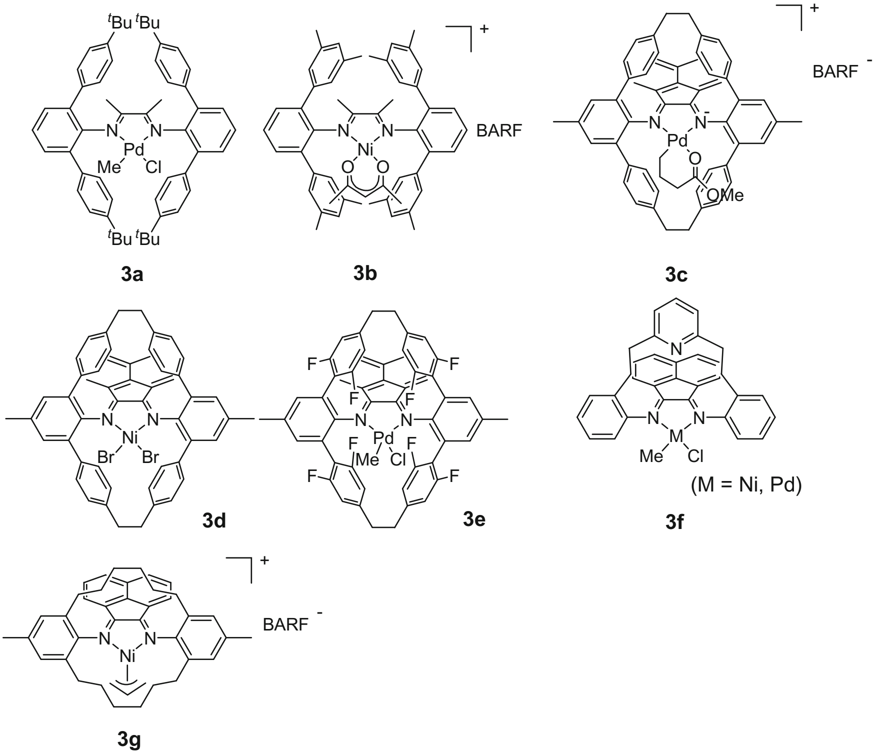


Chart 4.3 Modified diimine Pd and Ni complexes with bulky ligands

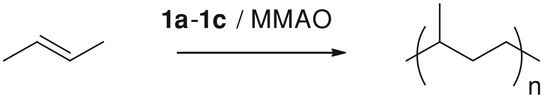
diimine Ni catalyst is deactivated under similar conditions. The catalyst is stable at elevated temperature also. The symmetric complexes having 2,6-diarylphenylimino groups affords almost linear polyethylene regardless of the polymerization condition, while unsymmetric complexes having 2,6-diarylphenylimino and mono- or non-substituted phenylimino groups at each nitrogen of the diimine ligand yields the polyethylene with branched structure [47, 48]. Thus, degree of branches of the produced polymer can be varied from low to moderate.

Guan designed the macrocyclic ligand by connecting the aryl substituents of 2,6-diarylphenylimino moieties by ethylene tethers. Their Pd and Ni complexes (Chart 4.3, **3c**, **3d**) have the two *N*-aryl groups with high coplanarity and show high catalytic activity (ca. 84 g/mmol h and 42,000 g/mmol h, respectively) [49]. The activity and molecular weight of the polymer are not decreased even in the polymerization at high temperature (70–90 °C). The diimine Ni complex with the macrocyclic ligand (**3d**) promotes living polymerization of propylene even at 50–75 °C [50]. Substituent of the ligand blocks axial site of the metal center and inhibits associative exchange of monomer and the vinyl-terminated polymer caused by β-hydrogen elimination. The catalyst enhances 2,1-insertion of the monomer and chain walking (straightening) reaction to form the polymer, whose branch density of the molecule is half of the polymer obtained by the conventional Ni-diimine complexes. Similar tendency is observed in the catalyst with fluorinated ligand (**3e**) [51]. Copolymerization of ethylene with acrylate using **3c** produced the polymer which contains the polar groups in higher content than the polymer obtained by **1f** [52, 53].

Connection of ortho carbons of two *N*-aryl groups by a pyridine-containing spacer forms the Pd and Ni complexes (**3f**), whose axial position is blocked by the pyridine group [54]. Polyethylene obtained by the catalyst has a smaller number of branches and higher molecular weights than that obtained by the usual Pd catalyst. The high molecular weight of the products is accounted for by the coordination of pyridine group to stabilize the cationic metal center and to depresses β-hydrogen elimination. In contrast, a similar macrocyclic Ni complex with oligomethylene tethers (**3g**) shows low activity [55].

4.2.1.3 Polymerization of Disubstituted Olefins

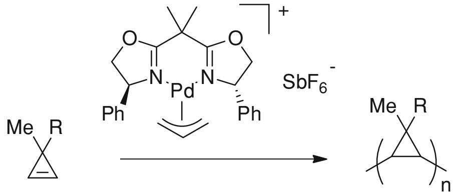
Diimine Ni complexes **1a**–**1c** promote polymerization of *trans*-2-butene in the presence of MMAO cocatalyst to afford the polymer with methyl branches (Eq. 4.5) [56]. The polymerization mechanism includes insertion of the monomer to CH_2–Ni bond and subsequent chain walking of the growing terminal to form a new CH_2–Ni bond. *Cis*-2-butene shows much lower reactivity for the polymerization [57]. Quantum mechanics calculations indicate that insertion of the *cis*-monomer to the Ni–C bond is suppressed by the steric interactions more significantly than the *trans*-monomer. The corresponding Pd complex is also active for the polymerization of *trans*-monomer only [58]. Higher insertion barrier of the *cis*-monomer compared to the *trans*-monomer was confirmed by direct observation of the reaction mixture by NMR. In addition to MMAO, Et_2AlCl is usable as the cocatalyst [59]. Although the polymer obtained by using the Ni complexes has atactic structure, Ni catalyst with C_2 symmetric structure **2b** in the presence of MMAO produces the isotactic polymer ($mm = 0.64$) [60].



(4.5)

Ni and Pd complexes with varieties of ligands have been reported to promote addition polymerization of norbornene to produce the high mass polymer. Hard β-hydrogen elimination of the norbornyl polymer end and ring strain of olefinic group of the cyclic monomer enhance smooth polymer growth. Details of the polymerization can be found in the previous review articles [61–63].

Cationic Pd complexes with N-N ligands, such as sparteine, bisoxazoline, and bipyridine, are effective for polymerization of cyclopropene in the absence of cocatalysts (Eq. 4.6) [64, 65]. In spite of its highly strained structure, the polymerization proceeds without expansion of the three-membered rings. Similar addition polymerization of cyclobutene derivatives also takes place by using cationic Pd complexes with phenanthroline ligands as the catalyst (Eq. 4.7) [66].



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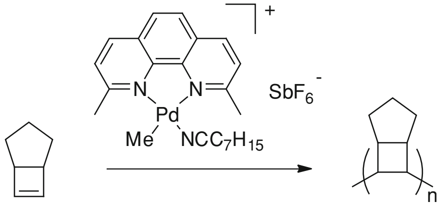

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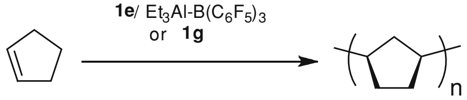
Pd- and Ni-catalyzed polymerization of cyclopentene produces the polymer with 1,3-*cis*-fused cyclopentane groups (Eq. 4.8) [67].

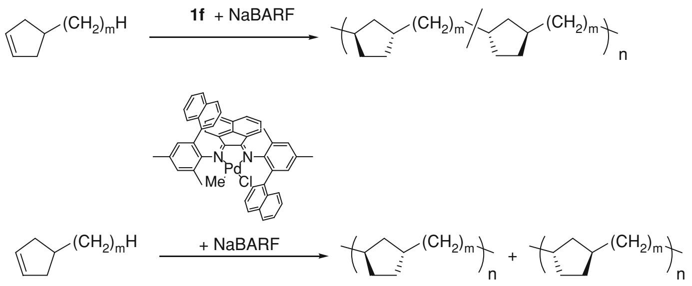


(4.8)

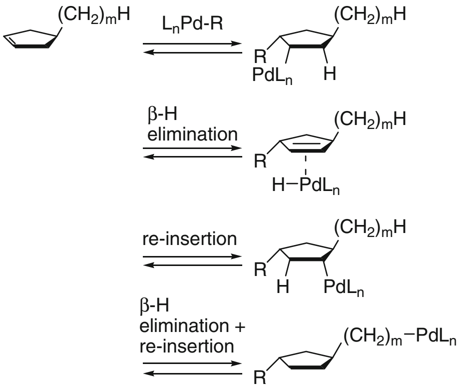
The tacticity of the polymer varies from atactic to isotactic ($rr = 66$ %), depending on the catalyst used.

The polymer with 1,3-*trans*-fused cyclopentane groups can be obtained by the Pd-catalyzed polymerization of 4-alkylcyclopentenes (Scheme 4.5) [68]. Similar to the polymerization of *trans*-2-butene, the mechanism of 4-alkylcyclopentenes includes insertion of the monomers to CH_2–Pd bond and chain walking of the Pd center to the terminal of alkyl groups (Scheme 4.6). Inversion of the Pd center with respect to the cyclopentane plane does not take place during the chain-walking reaction, resulting in the formation of *trans*-cyclopentane ring, selectively. C_2-symmetric Pd complex is effective for isospecific polymerization of those monomers to yield the corresponding polymers with high isotacticity ($rr > 93$ %).

The isotactic polymers, thus obtained, show liquid crystalline properties (Fig. 4.1). Although polyethylene has been reported to show liquid crystallinity at high temperature and under high pressure, the example of polyolefins showing



Scheme 4.5 Atactic and isotactic polymerization of 4-alkylcyclopentenes by diimine Pd complexes



Scheme 4.6 Mechanism of polymerization of 4-alkylcyclopentene

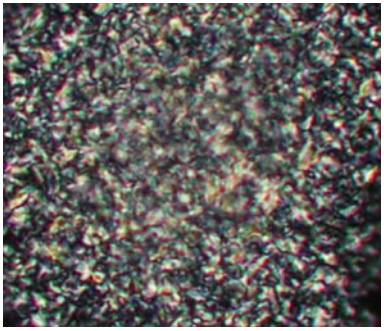


Fig. 4.1 Polarized optical micrograph of isotactic poly(4-ethylcyclopentene)

liquid crystallinity at ambient conditions have not been reported until recently [69, 70]. The range of liquid crystalline temperature can be varied by the spacers between cyclopentane groups in the polymer, which corresponds to the alkyl chain length of the monomer.

4.2.2 Cationic Complexes with Other Bidentate Neutral Ligands

In contrast to the Ni and Pd complexes with diimine ligands, those with iminopyridine ligands tend to show lower activity for ethylene polymerization in the presence of organoaluminum cocatalyst, and afford branched polyethylene with low molecular weight [71]. The ligand with pyridyl group having no bulky substituents enhances chain transfer reaction via β-hydrogen elimination. For example, the Ni complex with iminopyridine ligand having 2,6-diisopropylphenyl group (Chart 4.4, **4a**) shows moderate ethylene polymerization activity at 3.0–5.5 atm ethylene pressure, affording polyethylene with low to moderate degree of branching [72, 73]. Pd and Ni complexes with a 6-ethoxycarbonyl-2-iminopyridine ligand (**4b**) also promote polymerization of ethylene, but the product is a mixture of butene, oligoethylene, and polyethylene [74, 75]. It is not clear whether the ligand is bonded to the metal center in the *N*,*N*-bidentate form or the *N*,*N*,*O*-tridentate form with coordination of the ester group during the polymerization.

Pd complex with iminopyridine ligand having a long alkyl group at the imine nitrogen (**4c**) also promotes ethylene polymerization to produce polyethylene with a linear structure [76]. Ni complexes with azaferrocenylimine ligand (**4d**) and ligands with 2-methylphenyl or 2-isopropylphenyl groups at the coordinating nitrogen also catalyze ethylene polymerization [77]. Ni aminoimine [78] and aminopyridine [79] complexes are also active for ethylene polymerization to afford the branched polymer.

Jordan reported Pd complexes with bispyridyl methane ligand (**4e**) promote dimerization, oligomerization and polymerization of ethylene [80–82]. Although Ni complexes with diphosphine ligand tend to afford ethylene oligomer due to frequent chain transfer, the reaction using the nickel catalyst formed in situ from $Ni(cod)_2$, $H(OEt_2)_2BARF$, and bulky 1,2-bis[di(2-tolyl)phosphino]benzene yields relatively linear polyethylene in moderate yield [83]. Aminodiphosphine ligands are frequently used for Cr-catalyzed selective ethylene trimerization and tetramerization (Chap. 5) [84, 85]. The corresponding Ni complex (**4f**) is effective for ethylene polymerization [86]. Ni complex with bis(aminophosphine) and bis(aminophosphine oxide) ligands are proposed to prefer P-P and N-N coordinated form, respectively [87]. Both of the complexes are active for polymerization, although the products are a mixture of the oligomer and polymer. Ozawa and Yoshifuji prepared Pd complexes with bidentate phosphinidine ligands (**4g**) [88]. The complexes are thermally stable owing to metal-to-phosphorus π-back-bonding, and catalyze ethylene polymerization in the presence of $H(OEt_2)_2BARF$ to form the polymer with a linear structure. Ionkin also reported that the diphosphabutadiene Ni complex (**4h**) is thermally stable catalyst for ethylene polymerization [89].

Recently *N*-heterocyclic carbene ligands attract attention due to their high electron-donating character, bulky structure, and formation of the stable complex [90, 91]. Ni complexes with pyridyl-*N*-heterocyclic carbene ligands were

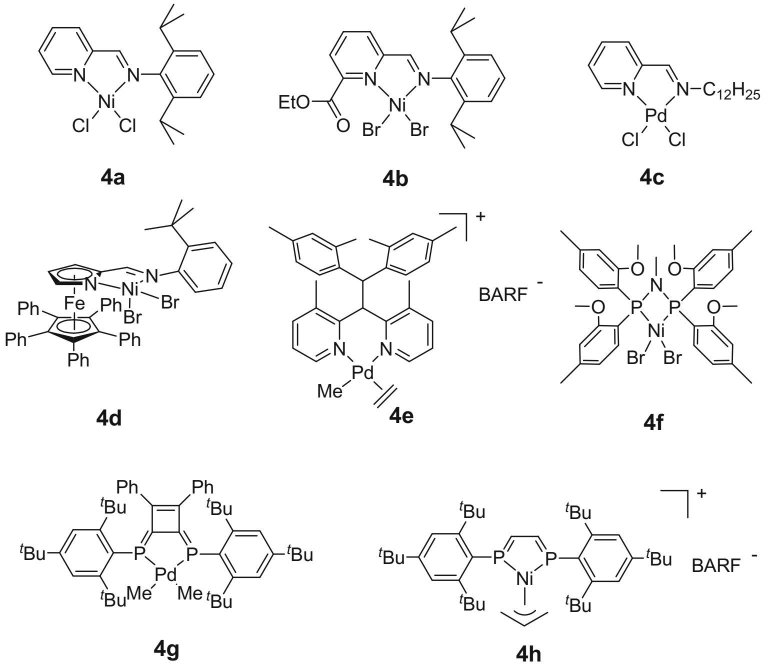


Chart 4.4 Pd and Ni complex catalysts with neutral ligands

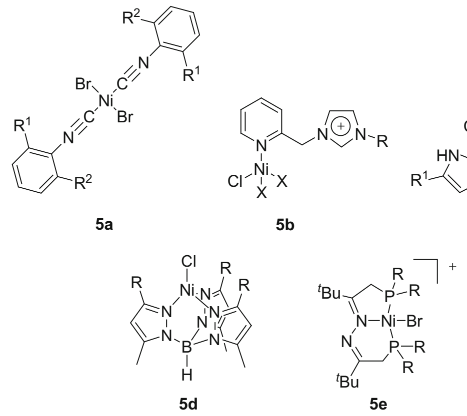
synthesized, where two bidentate ligands are coordinated to the metal center [92]. In the presence of MAO, it promotes ethylene polymerization to afford polyethylene having methyl branches.

4.2.3 Cationic Complexes with Monodentate and Tridentate Ligands

Ni and Pd complexes with monodentate and tridentate ligands were reported to catalyze ethylene polymerization. Ni complexes with arylisocyanide ligands (Chart 4.5, **5a**) [93] or a functionalized pyridine ligand (**5b**) [94] are active for ethylene polymerization in the presence of MAO. The produced polyethylene contains low to moderate degree of branches. In contrast, Pd and Ni complexes with pyrazole ligands (**5c**) in combination with MAO afford linear polyethylene due to very rapid ethylene insertion [95, 96]. It is noteworthy because most of the other cationic Pd complexes afford branched polyethylene.

Ni complexes with trispyrazolyl (**5d**) [97] and diphosphine azine (**5e**) [98] ligands promote ethylene polymerization in moderate to low activity to afford the branched polymer.

Chart 4.5 Pd and Ni catalysts with monodentate or tridentate ligands



4.3 Polymerization of Olefins by Neutral Pd and Ni Complexes with Monoanionic Ligands

The above-mentioned cationic complexes enabled high-mass polymerization of olefins because the monomer coordinates strongly to the electron-deficient metal center and undergoes smooth monomer insertion to the metal-polymer bond. On the other hand, SHOP process involves the neutral active species for ethylene oligomerization. Recently varieties of excellent neutral complex catalysts have been reported.

4.3.1 Neutral Complexes with Monoanionic N-O Ligands

4.3.1.1 Catalyst Having an Imine-Aryloxo (Phenoxyimine) Type Ligands

Salicylaldimine ligand, which is isoelectronic to enolate-phosphine ligand in SHOP process, forms Ni complex (Chart 4.6, **6a**, L = PPh_3). It promotes ethylene polymerization with addition of cocatalyst such as $Ni(cod)_2$ and $B(C_6F_5)_3$ [99] or without the additives [9]. Acetonitrile Ni complex (**6a**, L = MeCN) shows higher activity for ethylene polymerization than the PPh_3 complex [100]. The obtained polyethylene has low-to-moderate degree of branching (5–55 branches per 1,000 carbons). The complex with anthryl group in the ligand, **6b**, promotes dissociation of the ligand (L) to enhance coordination of the monomer, and to prevent deactivation of the catalyst via its disproportionation. Added $Ni(cod)_2$ scavenges the PPh_3 ligand to render the polymer growth smooth. The salicylaldimine Ni complexes with electron-withdrawing groups, such as 2-nitorophenyl and pentafluorophenyl groups, at the phenoxyimine ligand show higher catalytic activity [101].

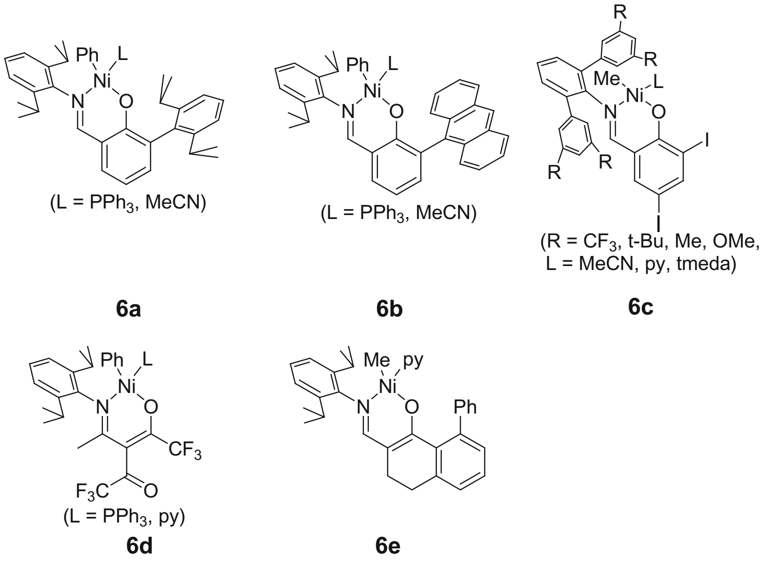
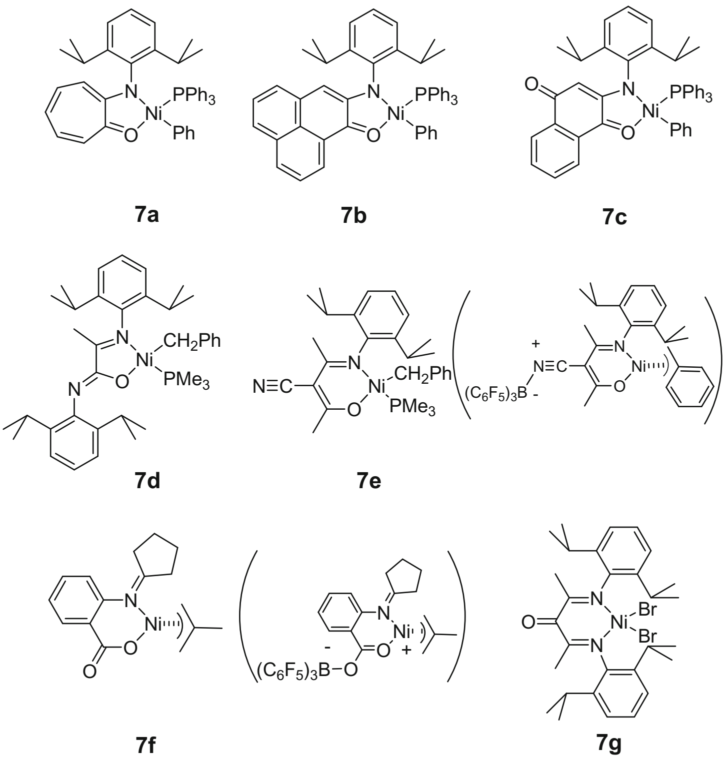


Chart 4.6 Ni catalysts with salicylaldimine ligands

High tolerance of the neutral complex toward polar functional groups enabled the polymerization in polar solvents as well as copolymerization of ethylene with olefins having ester, acetal, and diol groups which are apart from 2–8 carbons by a oligomethylene spacer [102].

Introduction of a bulky *N*-terphenyl group to the imine nitrogen (**6c**) is effective to ethylene polymerization [103, 104]. The *m*-substituents, R, despite remote positions from the Ni center, affect degree of branching and molecular weight of the produced polymer. The Ni complex catalyze the ethylene polymerization even in water (vide infra) and in supercritical CO_2 [105, 106]. The intermolecular reaction between alkyl-Ni complex and methyl- or hydride-Ni complex to form Ni bis(salicylaldimine) complex is regarded as a deactivation process of the catalyst [107]. Complex **6c** (L = tmeda) catalyzes dispersion polymerization of propylene and 1-butene under aqueous media [108]. Microstructure of the obtained polymer indicates 1,2-, 2,ω- and 1,ω- insertion of the monomer, similar to the polymerization catalyzed by Pd diimine complexes.

The complex having an imine-enolate ligand with electron withdrawing trifluoromethyl and trifluoroacetyl groups (**6d**, L = PPh_3) shows the high catalytic activity for a long period in the presence of $Ni(cod)_2$ or $B(C_6F_5)_3$, producing moderately-branched polyethylene (35–55 branches/1,000 °C) [109]. Similar anilinoenolate Ni complexes also promote copolymerization of ethylene with methyl methacrylate [110–113]. The complexes having ligand with acyclic structure require $B(C_6F_5)_3$ for the activation, whereas the complex of the ligand having



7a **7b** **7c**

7d **7e**

7f **7g**

Chart 4.7 Ni catalysts (or its precursor) with N-O chelating ligands. The activated form is in parenthesis

cyclic substituent (**6e**) acts as a single-component catalyst. Bulky substituents close to the alkoxy group improve the stability of the catalyst, although it does not influence activity of the catalysts.

4.3.1.2 Catalyst Having Tropone-Imide Type Ligands

Ni complexes with anilinotropone (Chart 4.7, **7a**) [114] or anilinoperinaphthenone (**7b**) [115] ligands polymerize ethylene. The reaction does not require cocatalyst, and the produced polyethylene contains low- to high degree of branches depending on the ethylene pressure during the polymerization.

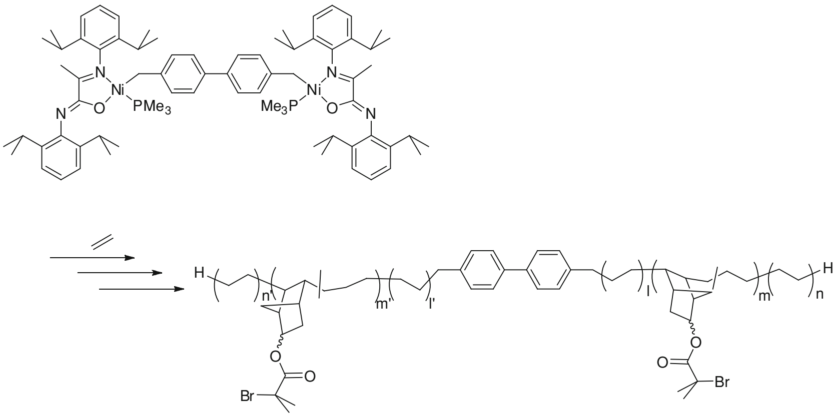
Detailed mechanistic studies revealed the chain-walking reaction during the polymer growth, similar to Pd and Ni diimine complexes [116]. Polyethylene with narrow molecular weight distribution can be obtained at low temperature [117].

Shiono reported that Ni complex with an aminonaphthoquinone ligand (**7c**) catalyzes ethylene polymerization, producing methyl branched polyethylene [118, 119]. Addition of $B(C_6F_5)_3$ leads to increase of the catalytic activity and produces polyethylene having short chain branches with moderate density. The proposed form of the catalyst has a zwitterionic structure, as mentioned in the next section.

4.3.1.3 Catalysts Having Imine-Hydroxo Type and Related Ligands: Zwitterionic Catalyst

Benzyl Ni complex with α-iminocarboxamide ligand (**7d**) is formed by the reaction of potassium salt of the carboxyamide with the Ni complex having a π-benzyl ligand [120]. The reaction with Ni(cod)$_2$ cocatalyst affords the phosphine-free intermediate, which catalyzes quasi-living polymerization of ethylene as well as copolymerization of ethylene with functionalized norbornene [121, 122]. Bulky aryl groups on both the nitrogens favor formation of the *N*,*O*-coordinated complex, which is active for ethylene polymerization [123, 124]. On the other hand, the complex with less bulky aryl group on either or both of the nitrogens prefers the *N*,*N*-coordinated structure, which shows low activity for ethylene oligomerization. Detailed studies on relevance of the complex structure and catalytic activity indicate that sterically bulky and electron deficient ligands result in increase in the activity and molecular weight of the produced polyethylene [125].

Addition of pyridine or 2,6-lutidine to the benzyl Ni complex with iminocarboxamide ligand yields the complex with pyridine (lutidine) by exchange of the phosphine ligand. In contrast, the reaction of Ni(cod)$_2$, potassium salt of the ligand, benzyl chloride, and pyridine affords the isomeric *N*,*O*-coordinated complex [126]. It acts as a single component catalyst for ethylene polymerization. The dinuclear Ni complex with bridging ligand causes ethylene polymerization at both Ni centers, and yields telechelic polyethylene as well as various triblock copolymers (Eq. 4.9) [127].



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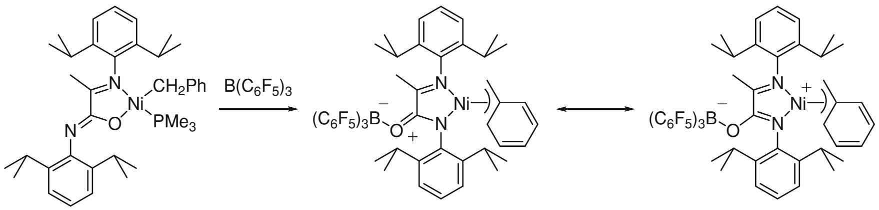


Scheme 4.7 Formation of zwitterionic catalyst

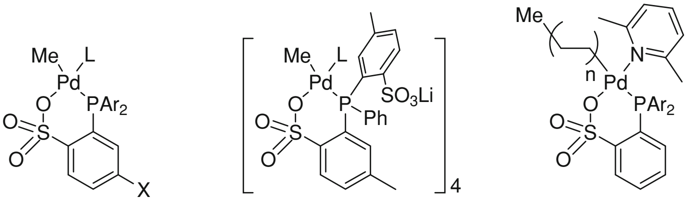
Bazan reported that the α-iminocarboxamide Ni complex in combination with $B(C_6F_5)_3$ and R_3Al catalyzes ethylene polymerization [120, 128, 129]. The cocatalyst not only abstracts the phosphine ligand from the Ni center, but also forms a bond with the oxygen atom of the ligand to afford a zwitterionic Ni complex with an *N*,*N*-chelating ligand (Scheme 4.7).

A canonical structure (Scheme 4.7 right) has coordination of the diimine ligand to the Ni center, similar to the structure of the active species of the Brookhart's diimine Ni catalyst [130]. The complex catalyzes ethylene polymerization to produced polyethylene with a branched structure (33–106 branches per 1,000 carbons). Ni complex with β-anilinoenolate ligand having a nitrile group (**7e**) also affords the zwitterionic complex by addition of $B(C_6F_5)_3$, which forms a $C{\equiv}N^+\text{-}B(C_6F_5)_3^-$ bonding. The produced complex catalyze ethylene polymerization without addition of co-catalyst [131]. Zwitterionic complex formed by the reaction of $B(C_6F_5)_3$ with (2-(alkylideneamino or diphenylamino)benzoate)nickel complex (**7f**) promotes dimerization or polymerization depending on the *N*-substituents [132].

Ni complexes with β-diimine ligands is unreactive for ethylene polymerization in spite of high activity of the α-diimine complexes [133]. In contrast, Ni complex with α-keto-β-diimine ligand (**7g**) shows much higher activity (ca. 700-fold increase compared to β-diimine complex) [134–136]. Coordination of organoaluminum to the carbonyl group enhances the catalytic activity. The catalyst is also active for propylene and 1-hexene polymerization. These polymerization reactions using MAO cocatalyst proceed in living fashion to afford the polymer with narrow molecular weight distribution. The polyethylene obtained by the catalyst shows only isolated methyl branches (16 branches per 1,000 carbons) and semicrystalline properties. The polypropylene produced by the catalysts also shows only methyl branches and rich in isotactic sequence (m = ca. 77 %). Effect of $B(C_6F_5)_3$ for anilinotropone complex (**7c**) is also attributed to the zwitterionic catalyst [118, 119].

4.3.2 Phosphinesulfonate Complexes of Pd

Pd complexes with phosphinesulfonate ligands (Chart 4.8, **8a**, Ar = Ph, 2-EtC_6H_4, 2-$MeOC_6H_4$, 2-(2'6'-$Me_2C_6H_3$)C_6H_4, X = H, Me, L = pyridine, lutidine, tmeda, dmso) have attracted recent attention as the catalyst for ethylene polymerization and



8a **8b** **8c**

Chart 4.8 Pd phosphinesulfonate catalysts

copolymerization. The catalysis was originally found by Drent and Pugh, who reported that Pd(dba)$_2$ or Pd(OAc)$_2$ in combination with the ligand promote copolymerization of ethylene with acrylate, to produce the polymer containing acrylate repeating units in the main chain [137]. It also enabled non-alternating copolymerization of ethylene with CO [138]. Then, Rieger and Nozaki isolated Pd-phosphinesulfonate complexes having a pyridine, lutidine, or dihydrodicyclopentadienyl ligand, which also catalyze the copolymerization with high efficiency [139, 140].

The phosphinesulfonate Pd complexes act as single-component catalyst for ethylene polymerization. One of the significant characteristics of the catalysis is their activity for copolymerization of ethylene with wide varieties of polar functionalized olefin monomers (See Chap. 6). The other is the formation of linear polyethylene in the ethylene polymerization, which is uncommon in the cationic Pd catalysts [141–144]. In contrast to most of the late transition metal catalysts, introduction of bulky substituents on phosphine leads to decrease of the catalytic activity and molecular weight of the polymer [145]. The Pd complex with pendant lithium arylsulfonate group (**8b**) adopts a tetranuclear structure [146]. The complex is not soluble in common organic solvent, but affords high molecular weight polyethylene with broad molecular weight distribution. Addition of pyridine derivative to the solution of tetranuclear complex causes its dissociation to the mononuclear one, which is soluble in toluene and insoluble in hexane. As the mononuclear complex affords high molecular weight polyethylene only in hexane, the heterogeneity of the reaction mixture plays an important role.

Theoretical studies rationalized the formation of linear polyethylene. Ziegler reported high energy barrier of β-hydride elimination and subsequent chain branching in the ethylene polymerization catalyzed by the Pd phosphinesulfonate complex [147]. Recently, Morokuma and Nozaki reported comprehensive results of their experimental as well as theoretical study on the mechanism of ethylene polymerization catalyzed by the complex [148]. They actually isolated alkyl Pd complex (**8c**) by the transmetalation reaction of chloropalladium complex and trialkylaluminum. The complex is stable in solution, but undergoes partial dissociation of lutidine, forming agostic interaction of β- or γ-hydrogen of the alkyl ligand. The methylpalladium complex promotes isomerization of 1-hexene to 2- and/or 3-hexene, probably via the alkyl Pd species which undergoes β-hydride elimination and re-insertion of the olefins. β-Hydrogen elimination is favored under low concentration of ethylene, and applying sufficient ethylene pressure to the reaction mixture makes the chain propagation dominant over β-hydrogen elimination.

The Ni-phosphinesulfonate complexes are also synthesized and used as the catalyst for ethylene polymerization. Ni-allyl [149], Ni-benzyl [150], and Ni-Me [151] complexes afford branched polyethylene with low molecular weight in toluene. In contrast, Ni-Me complex affords linear high molecular weight polyethylene in heptane or 1-octene [151]. The catalyst is stable for hours at 90 °C during the polymerization. Very low solubility of the complex in those solvents is proposed as an important technical reason for formation of the high molecular weight polymer.

4.3.3 Neutral Complexes with Other Monoanionic Ligands

Since the discovery of salicylaldimine Ni complex catalysts, Ni complexes with varieties of monoanionic N-O, N-N, and P-O ligands have been reported. Ni complex with ortho-formylanilide ligand [152] is less active for ethylene polymerization. Although the complex with iminopyridine N-oxide ligand (Chart 4.9, **9a**) [153] appears to be a neutral ligand, active species formed from the corresponding Ni complex contains the *N*,*O*-chelating ligand, similarly to the salicylaldimine Ni complex. It actually shows high activity for ethylene polymerization and is effective also for ethylene-methyl acrylate copolymerization.

Ni complexes with monoanionic N-N ligands such as β-diketiminate (**9b**) [154], iminoanilido [155], and iminosulfonamido (**9c**) [156] catalyze ethylene polymerization only in the presence of MAO. Waymouth reported Ni complex with N-heterocyclic carbene enolate ligand (**9d**) acts as a single component catalyst for ethylene polymerization [157]. The activity is low to moderate to yield the linear polymer with molecular weight M_n ranging from 1,000 to 7,100. In addition to the above studies, Longo reported that Cp_2Ni in combination with MAO promotes ethylene polymerization to afford polyethylene with high molecular weight and high melting point [158]. The active species of the polymerization catalyst, however, is unclear.

In 1981, Keim reported that Ni complex with aminobis(imino)phosphorane ligand (**9e**) is effective for ethylene polymerization [159]. Later on, Fink found that the catalysts promote selective 2,ω-polymerization of α-olefins to give the polymer with methyl branch [160, 161]. It is accounted for by the selective 1,2-insertion of the monomer and chain walking during the polymer growth. Such polymerization takes place only the ligand contains $SiMe_3$ substituents at the coordinating nitrogen. Recently, Ni complexes with iminophosphonamide ligands (**9f**) were synthesized [162, 163]. Although the isolated complexes are inactive for ethylene polymerization, the catalysts prepared in situ by mixing the ligands and $Ni(cod)_2$ or $Ni(allyl)_2$ afforded branched polyethylene.

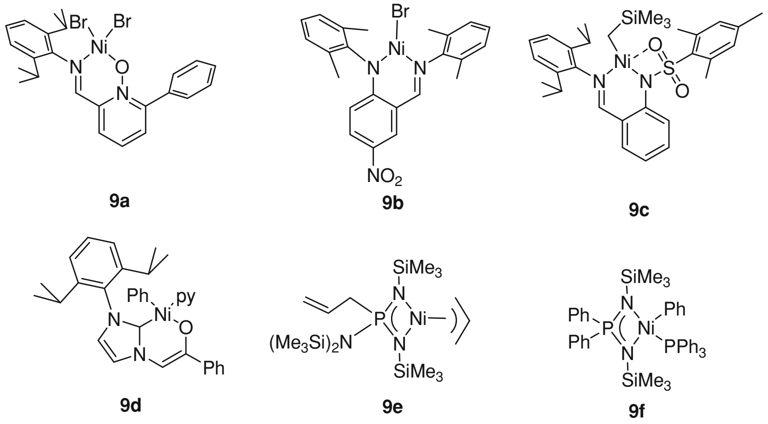


Chart 4.9 Ni and Pd catalysts with monoanionic ligands

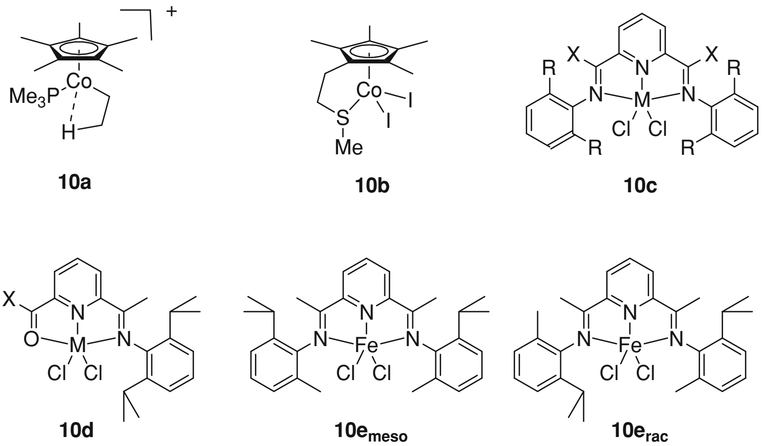
4.4 Polymerization of Olefins by Fe and Co Complexes

Brookhart reported cationic half cobaltcene complex (Chart 4.10, **10a**) shows activity, though not high, for ethylene polymerization in 1985 [164]. The polymerization proceeds in living fashion to afford polyethylene with narrow molecular weight distribution even in the absence of cocatalyst [165]. Aryl and silyl terminated polyethylenes can be synthesized by using benzyl and silylmethyl cobalt complexes as the respective initiator [166]. The activity is improved recently by sulfur-containing half cobaltcene complex (**10b**) [167]. Similar half-sandwich Co complexes with quinoline or *N*,*N*-dimethylaniline moieties are reported as the catalyst with low activity [168].

In 1998, Fe and Co complexes with bis(imino)pyridine ligands (**10c**) were reported to show very high catalytic activity ($>10^5$ g/mmol h bar) (especially Fe catalyst) for ethylene polymerization, producing polyethylene with a linear structure [6–8, 169–171]. The complexes are used in combination with organoaluminum co-catalyst. Generally, activity of the Fe catalyst is higher in one to two order of magnitude than Co catalyst under similar conditions. Similar to the diimine Ni and Pd complex catalysts, the complexes with arylimino groups having substituents on ortho position are favorable for high catalytic activity.

Those bulky substituents make the aryl plane perpendicular to the bis(imino)pyridine plane, and suppress the chain transfer reaction effectively. The complexes with less bulky arylimino groups tend to form oligomer of ethylene, rather than polyethylene [172–174]. The complexes with aldimine structure (**10c**: X = H) show lower activity than those with ketimine structure (**10c**: X = Me). Various organoaluminums, such as $AlMe_3$, $AlEt_3$, $AlEt_2Cl$ in addition to MAO and MMAO, are usable as the cocatalyst.

β-Hydride elimination is the only chain-transfer pathway in the Co-catalyzed polymerization, and the produced polymer has a vinyl group at the terminating



10a **10b** **10c**

10d **10e$_{meso}$** **10e$_{rac}$**

Chart 4.10 Fe and Co complex catalysts

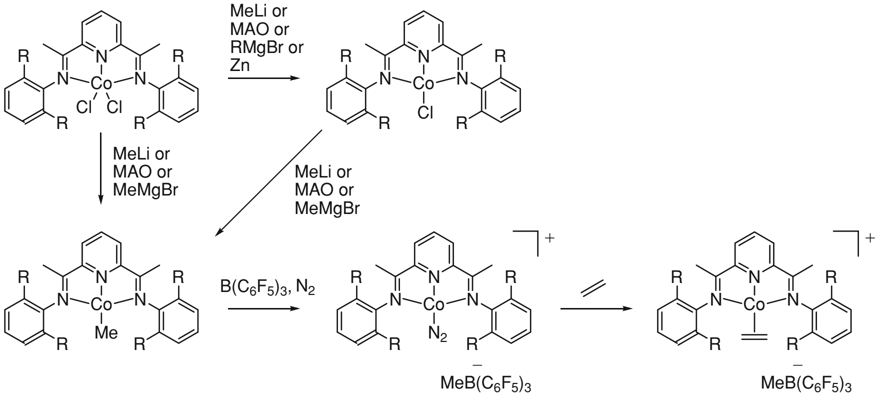
end. The Fe-catalyzed polymerization involves β-hydride elimination as well as transmetalation with organoaluminum cocatalyst as the chain-transfer reaction, giving the polymers having a vinyl or alkyl terminating end. The Fe-catalyzed ethylene polymerization in the presence of R_2Zn, which is a more efficient chain transfer reagent than the alkylauminum compounds, causes frequent transmetalation between the growing species and organozinc compounds [175–177]. Further details are mentioned in Chap. 5.

The active species of the polymerization is initially considered to be cationic alkyl metal species, similar to the metallocene polymerization [178, 179]. Detailed characterization of the active species and theoretical studies, however, clarified unique polymerization mechanism. In the Co-catalyzed polymerization, Co(II) procatalyst is firstly reduced to Co(I) [180, 181]. Subsequent reaction with $B(C_6F_5)_3$ produces the cationic Co(I) species. Nucleophilic attack of the abstracted alkyl group to the coordinated monomer gives alkyl Co(I) species with dinitrogen or ethylene ligand (Scheme 4.8).

Actually, the isolated Co(I) alkyl complex promotes ethylene polymerization without addition of cocatalyst.

The active species of the Fe-catalyzed polymerization is rather complicated due to facile valence change and flexible coordination structure of the penta-coordinated metal center. EPR and Mössbauer analysis [182] and detailed ^1H and ^2H NMR as well as EPR studies [183–185] revealed the active species formed by the reaction of Fe complex with various organoaluminums (Scheme 4.9).

Initially proposed structure of intermediate, **A**, was modified as mentioned below. Reaction of Me_3Al-free-MAO with the Fe(II)Cl_2 complex produces [(bis(imino)pyridine)Fe(II)(μ-Cl)(μ-Me)$AlMe_2$]$^+$[Me-MAO]$^-$ (**B**) (Al/Fe $<$ 200) and [(bis(imino)pyridine)Fe(II)(μ-Me)$_2$$AlMe_2$]$^+$[Me-MAO]$^-$ (**C**) (when Al/Fe $>$ 500). The reaction in the existence of Me_3Al or $^tBu_3Al$ gives neutral

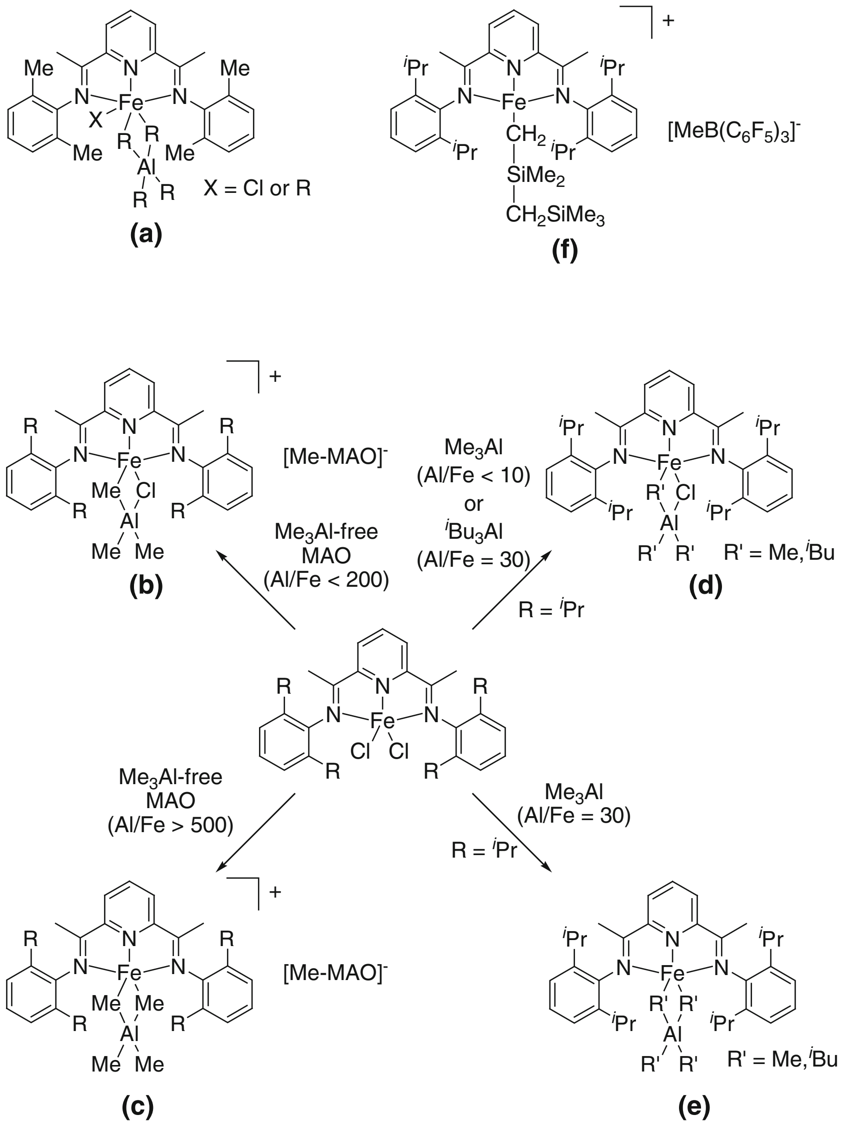


Scheme 4.8 Synthesis of intermediate of the Co-catalyzed ethylene polymerization

intermediate [(bis(imino)pyridine)Fe(II)(Cl)(μ-R)$_2$AlR$_2$] (**D**) or [(bis(imino)pyridine)Fe(II)(R)(μ-R)$_2$AlR$_2$] (**E**). Repo conducted electrospray ionization tandem mass spectrometric analysis of the active species formed from bis(imino)pyridine Fe complex and MAO, and observed cationic Fe(II)X species (X = Me, Cl, H) [186]. Chirik succeeded in isolating cationic Fe(II) complex [(bis(imino)pyridine)Fe(II)-(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)]$^+$[Me-B(C$_6$F$_5$)$_3$] (**F**). The complex actually initiates ethylene polymerization without cocatalyst, although its activity is lower than the catalyst formed in situ by mixing (bis(imino)pyridine)Fe(II)Cl$_2$ and MAO [187]. The polyethylene formed by bis(imino)pyridine Fe catalyst shows a broad or multimodal GPC pattern suggesting to wide molecular weight distribution [188]. It is proposed probably due to the presence of multiple active species, a short-lived highly active centers producing low molecular weight polymer and a long-lived less active centers producing high molecular weight polymer.

Varieties of modified bis(imino)pyridine Fe and Co complexes have been reported [169]. They include the complexes with various substituents on the arylimino group or with different donor moieties in place of pyridine and/or imine. Most of the reported complexes afford linear polyethylene, whereas those with large aromatic groups on the imino group cause formation of polyethylene with methyl and ethyl branches [189].

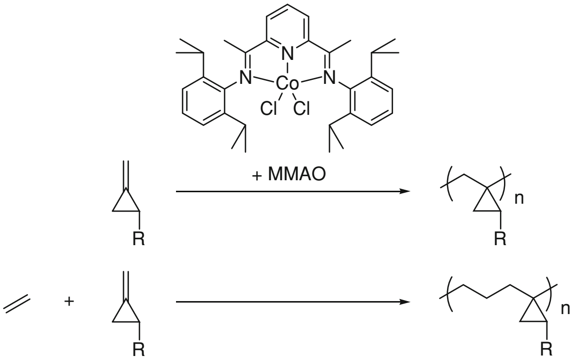
Fe and Co complexes with bidentate *N*-ligands such as α- and β-diimine [190], bisoxazoline, and sparteine [191] are much less active for ethylene polymerization, and afford low molecular weight oligomer. Combination of bis(imino)pyridine CoMe complex and Li[B(C$_6$F$_5$)$_4$] promotes ethylene polymerization with low activity [192]. Coordination of Li ion to imino nitrogen is proposed. Fe complex with 2-acetyl-6-iminopyridine ligand (**10d**, M = Fe, X = COMe) promotes ethylene polymerization to yield the branched polymer [193]. Similar Co complex with 2-ethoxycarbonyl-6-iminopyridine ligand (**10d**, M = Co, X = COOEt), in contrast, affords a mixture of the oligomer and polymer with linear structure [194].



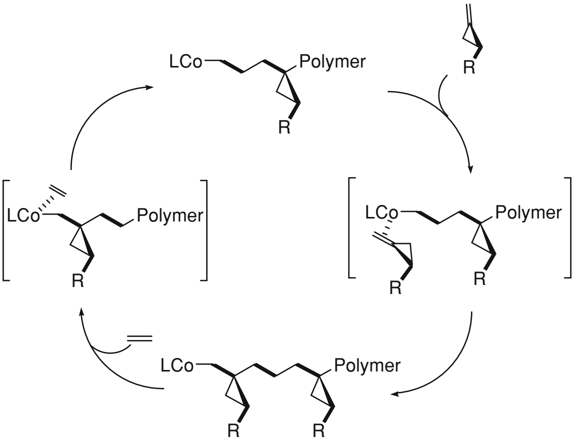
Scheme 4.9 Synthesis of intermediates of the Fe-catalyzed ethylene polymerization

Fe complexes with bis(imino)pyridine ligand are also active for propylene polymerization. The polymerization produces isotactic polypropylene via 2,1-insertion of propylene chain-end control mechanism [195]. Fe complex with 2-isopropyl-6-methylphenylimino group exists as a mixture of *racemo*- and *meso*-stereoisomers (**10e**$_{\text{rac}}$, **10e**$_{\text{meso}}$). Campora succeeded in isolating these isomers and employed them as the catalyst for propylene polymerization [196]. Both complexes afford isotactic polypropylene, although the meso complex shows higher activity than racemo complex. The *rac*-isomer affords polypropylene with slightly

Scheme 4.10 Co-catalyzed polymerization of methylenecyclopropanes



Scheme 4.11 Mechanism of Co-catalyzed copolymerization of ethylene with methylenecyclopropanes



increased isotactic pentad, indicating cooccurance of enantiomorphous site control and chain-end control.

The Fe and Co catalysts do not afford polymers of 1-butene, but its dimers composed of inner C8-olefins with linear structure (see Chap. 5) [174, 197]. The formation of the dimer is accounted for by the initial 1,2-insertion of the olefin into metal-hydrogen bond, subsequent 2,1-insertion of the olefin into metal-carbon bond, and β-hydrogen elimination of the alkyl-metal species to regenerate hydride metal species.

Although Co catalyst is not active for α-olefin polymerization, it can promote polymerization of methylenecyclopropane, a disubstituted olefin with strained three-membered ring, very efficiently (Scheme 4.10) [198–200].

The produced polymer has three-membered ring in every repeating unit. The polymerization at −40 °C proceeds in living fashion, affording the polymer with narrow molecular weight distribution. It is speculated that the polymerization proceeds via selective 1,2-insertion of the monomer because of the bulky cyclopropylidene group. The absence of β-hydrogen in the growing chain end is accounted for the living chain growth.

The catalyst also promotes alternating copolymerization of ethylene with methylenecyclopropane to afford the polymer with three membered ring in every four carbons unit in the main chain (Scheme 4.11).

4.5 Polymerization of Olefins by Other Late Transition Metal Catalysts

In 1992, cationic Rh complex with triazacyclononane ligand (Chart 4.11, **11a**) was found to be active for ethylene polymerization in aqueous media [201, 202]. Although the activity of the catalyst is very low, the complex acts as a single component catalyst. Pt complex with structurally similar trithiacyclononane ligand (**11b**) also promotes ethylene polymerization in the presence of MAO [203]. Recently, Rh complex (**11c**) with high activity was reported by Jin [204]. He also reported complexes of the metal centers that are not common in olefin polymerization catalysts, such as Ag (**11d**) [205] and Ir (**11e**) [206]. All of these complexes are used in combination with MAO. It is not clear whether the produced polymer is of linear or branched structure.

Although Fe and Co complexes with bis(imino)pyridine ligands are active for ethylene polymerization, the corresponding complexes of transition metals of the same ligand, Ru and Rh, show no catalytic activity [207]. In contrast, Nomura reported that Ru complex with pybox ligand (**11f**) promotes ethylene polymerization as well as ethylene/1-hexene copolymerization [208]. The polyethylene contains no branches. The corresponding Fe analogue catalyzes ethylene polymerization, but is not active for copolymerization of ethylene with 1-hexene, giving ethylene homopolymer with linear structure [209].

Copper complexes with diimine and phenoxyimine ligands were reported to catalyze homopolymerization of ethylene and methyl methacrylate as well as the copolymerization of these monomers [210–213]. More recent investigation of the reaction, however, revealed that the aluminum complex, formed by the ligand exchange between the catalyst and cocatalyst, acts as the active species in all these polymerizations [214].

4.6 Multimetallic Catalysts

Single site catalyst has its advantage in the synthesis of polymers with regulated molecular weights and structures. In synthetic organic reactions, the catalysts containing two or more active centers are employed with the expectation of synergistic effects of two close active metal centers in the catalysts and/or possible occurrence of tandem reactions promoted by those active centers. Polymerization of olefins by using di- or multinuclear catalyst also attracts recent attention [215].

Dinuclear Ni catalysts having salicylaldimine ligands (Chart 4.12, **12a**–**12c**) have been reported to show higher catalytic activity for ethylene polymerization

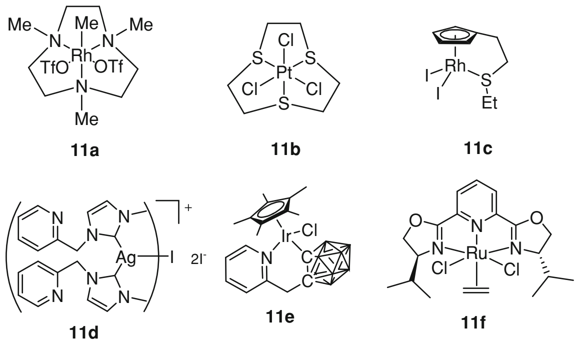


Chart 4.11 Late transition metal catalysts other than Ni, Pd, Fe, and Co

and/or to produce polyethylene with higher molecular weight compared to the mononuclear analogue [216–220]. The higher activity of the dinuclear catalysts is accounted for by the increased rate of insertion of the monomer as a result of steric bulkiness and electronic effect of the dinuclear structure. The polyethylene obtained by **12c** also shows increased selectivity in methyl-branched structure compared to the mononuclear complex [220]. Dinuclear salicylaldimine Ni complexes **12a** and **12c** promote copolymerization of ethylene with acrylates and/or norbornene with polar functional group to give the copolymer with high content of the comonomer unit [221, 222]. The proximal Ni center is proposed to facilitate smooth insertion of the comonomer via coordination of the functional group to the Ni center. Dinuclear Fe and Co complexes with bis(imino)pyridine ligands also show higher catalytic activity than the mononuclear complex probably due to the steric and/or electronic effects [223, 224].

Trimetallic Fe complexes with cyclic bis(imino)pyridine ligands [225] and tetranuclear Ni catalyst based on linear oligodiimine ligand [226] show higher catalytic activity and/or longer lifetime than the mononuclear complex, although the cooperation mechanism of the metal centers is not clear. Tetra-, octa- and hexadecanuclear pyridylimine Ni complexes having similar dendritic ligands with 1st, 2nd and 3rd generations (**12d**) are reported [227]. As the generation and nuclearity increase, the product with less molecular weight and less degree of branches is formed.

Although homo-dinuclear complexes usually afford the complex catalyst with two similar active sites, hetero-dinuclear complexes are expected to yield that with different active sites. Nagashima reported Ni-Co and Ni-Fe heterodinuclear complexes (**12e**), which show higher catalytic activity than the mononuclear Ni complex [228, 229]. The Ni center within the metalacycle is proposed to increase planarity of the diimine ligand bonded to the metal center. Although the polymers obtained by the Ni-Co and Ni-Ni catalysts are of unimodal molecular weight distribution, that obtained by Ni-Fe complex is bimodal, due to the independent polymerization at the Ni and Fe centers.

Cross-metathesis reaction of Zr and late transition metal complexes produces Zr-Pd, Zr-Co and Zr-Ni heterodinuclear complexes (**12f**) [230]. Although Zr-Pd complex is not active for ethylene polymerization, Zr-Co complex produces

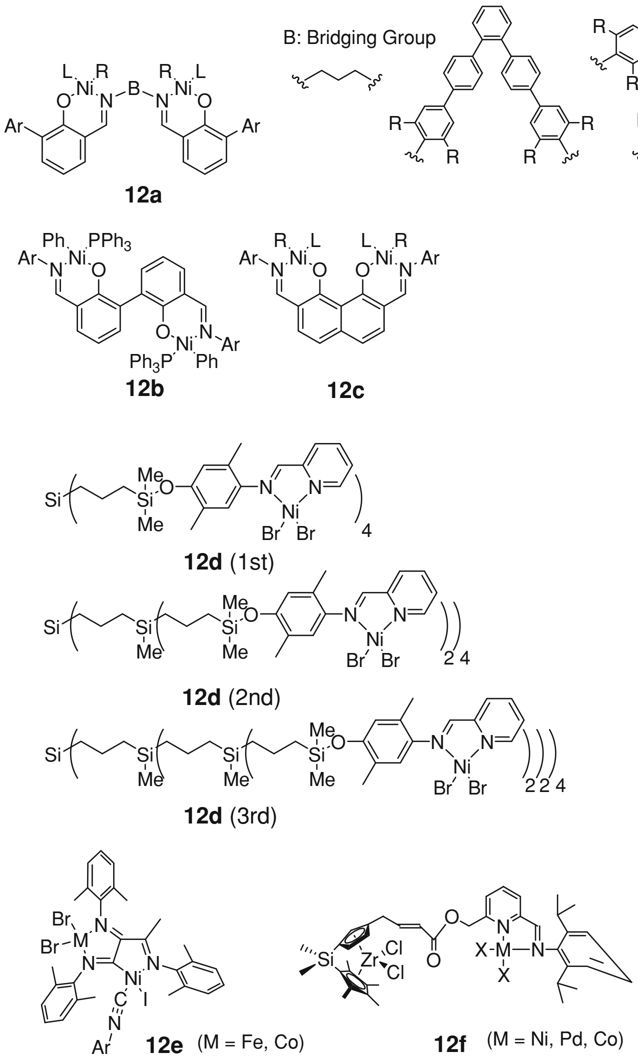
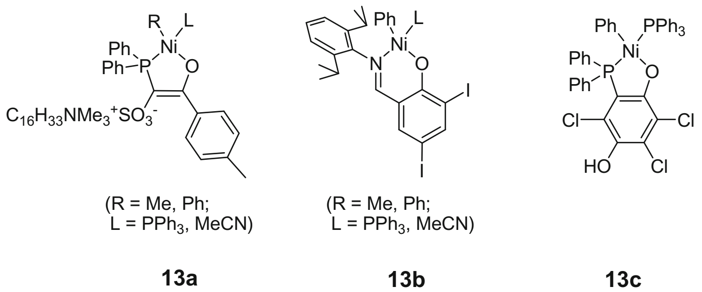


Chart 4.12 Dinuclear and multinuclear complex catalysts

polyethylene having Et branch exclusively. Zr-Ni complex is also effective for the polymerization to give the polymer with Me, Et, and long chain branches. Co and Ni centers promote dimerization and oligomerization of ethylene, respectively, and the vinyl-terminated ethylene oligomers, thus formed are considered to be copolymerized effectively with ethylene on the Zr center.



13a **13b** **13c**

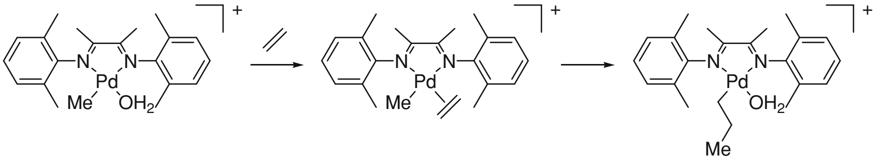
Chart 4.13 Ni catalysts for ethylene polymerization in aqueous media

4.7 Olefin Polymerization in Aqueous Media

As late transition metal complexes are rich in *d*-electron, even the corresponding cationic complexes have low Lewis acidity and their catalytic activity is not influenced largely by coexistence of polar molecules. The high tolerance toward polar molecules enabled ethylene polymerization in aqueous media [231, 232].

Ethylene polymerization in aqueous media has been reported by using single-component Rh catalyst **11a** [201, 202]. Mecking found that both cationic diimine Pd complexes as well as neutral Ni complexes catalyze ethylene polymerization in water. The polyethylene obtained by diimine Pd catalyst (**1f**) is rubbery and shows lower degree of branching and higher molecular weight, when compared to the oily polymer obtained in organic solvent [233]. Diimine Pd complex is stable during the polymerization because of the encapsulation of the catalyst in water by hydrophobic amorphous polymer. The catalyst is actually decomposed in acetone/water solution containing ethylene.

Neutral Ni complexes with phosphinoenolate or salicylaldimine ligands (**13a**, **13b**) also promote ethylene polymerization in water [234]. The activity is again lower than the polymerization in organic solvent, which is due to the lower ethylene concentration in water. The Ni complex catalysts are stable in water for hours. Similar neutral salicylaldimine Ni complex with terphenyl structure (**6b**) promotes ethylene polymerization in the presence of surface activating agent such as sodium dodecylbenzenesulfonate (20–40 ethylene pressure, 50 °C) [113]. Rate of the polymerization in water is generally lower than in organic solvent. In contrast, the above water-soluble complex shows higher catalytic activity in water than in toluene [235, 236]. The enhanced activity in water is accounted for by the efficient scavenging of the hydrophilic coordinating ligand in water. The polyethylene produced by the catalyst forms extremely small particles. It is proposed that each complex catalyst forms one polyethylene particle. The catalysts are also active for ethylene/1-butene copolymerization [237] as well as homopolymerization of propylene, 1-butene, and 1-hexene [118] in water. Ni complexes with enolateimine ligands (**6d**, L = py) also promote ethylene polymerization in aqueous media [238] (Chart 4.13).



Scheme 4.12 Ligand exchange and ethylene insertion of the Pd catalyst in water

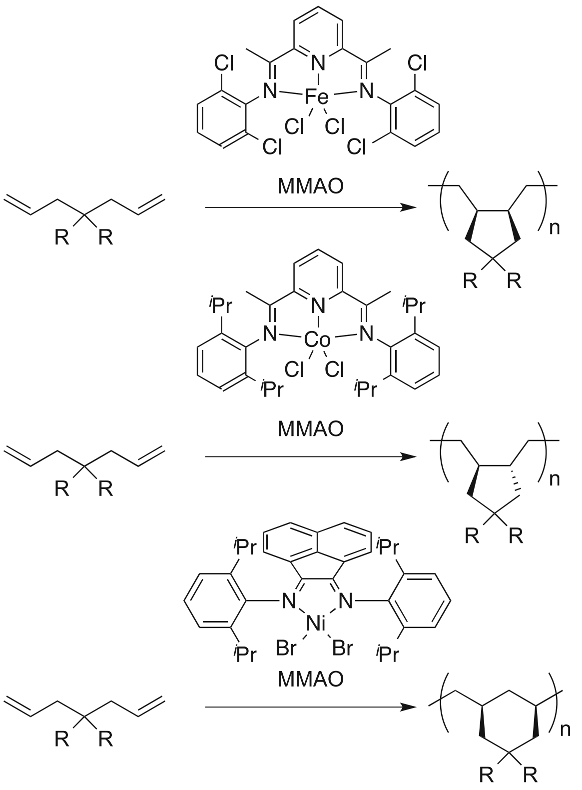
Although complexes with electron deficient substituents tend to result in decomposition via hydrolysis or coordination of water, the catalyst are stable in water at 70 °C for hours. The water-soluble catalyst affords polyethylene whose crystallinity and melting points are controlled in wide range (crystallinity = <25–50 %, T_m = 75–129 °C) as particles [239].

Ni complex with a P-O ligand (**13c**), which is formed in situ by mixing commercially available *p*-chloranil, PPh_3, and $Ni(cod)_2$, also bring about ethylene polymerization in aqueous media to form polyethylene particle [240]. The polymerization in the presence of cationic surfactant, dodecyltrimethylammonium bromide (DTAB) affords polyethylene with extremely small polyethylene particle with a diameter of 11–16 nm [241]. Similar polyethylene particle with small size can also be accessible by using water-soluble complex with sulfonate moiety [242]. The aqueous ethylene polymerization in the presence of silica particle leads to silica-polyethylene nanocomposite particle [243]. Water-soluble Pd complex with phosphinesulfonate ligand is active for ethylene polymerization in water, but its activity is lower than that in toluene [244].

Experimental and theoretical studies on the aqueous ethylene polymerization have been reported. Diimine Pd and salicylaldimine Ni complexes are stable toward hydrolysis and water does not interfere the coordination and insertion of ethylene to metal-carbon bond (Scheme 4.12) [245, 246]. Coordination of ethylene molecule to cationic diimine Pd aqua complex and subsequent insertion to its Pd-carbon bonds are directly observed by NMR. The diimine Pd complex is decomposed in the presence of ethylene in water because Wacker-type reaction takes place and generates Pd(0) species [247]. The plausible deactivation pathway for salicylaldimine Ni complex is the formation of bis(salicylaldimine) complex by the reaction of alkyl-Ni complex and methyl- or hydrido-Ni complex.

4.8 Cyclopolymerization of Non-conjugated Dienes

Polymerization of non-conjugated dienes, especially 1,5-hexadiene, is accompanied by ring closing of the monomer on polymerization to give the polymer with cycloalkane groups. Early transition metal complexes have been extensively used as the catalyst for the cyclopolymerization [248]. These complexes allow 1,2-insertion of a vinyl group and subsequent cyclization by 1,2-insertion of the remaining vinyl group. The obtained polymer mostly contains both *trans*- and *cis*-1,3-cyclopentane groups.

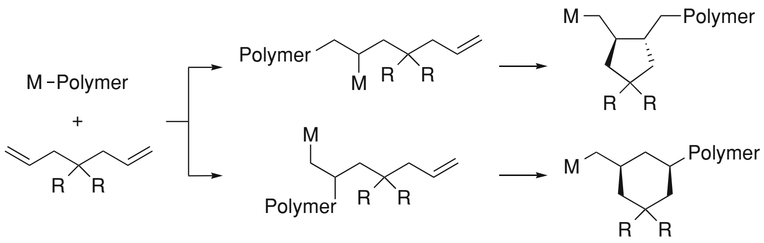


Scheme 4.13 Cyclopolymerization of 1,6-hetpadienes by Fe, Co, and Ni catalysts

Recently, late transition metal complexes were revealed to promote stereoselective polymerization of 1,6-heptadienes [249]. Fe and Co complexes with bis(imino)pyridine ligands (**10c**) bring about polymerization of 1,6-heptadiene to give the polymer having *cis*- or *trans*-1,2-cyclopentane structure, selectively (Scheme 4.13) [250, 251]. These catalysts are also applicable to the polymerization of 4-siloxy-1,6-heptadiene, 4-phenyl-1,6-heptadiene, and 9,9-diallyfluorene.

Co complex brings about copolymerization of 1,6-heptadiene with ethylene to give the polymer with *trans*-1,2-cyclopentane groups [252]. The copolymers rich in the repeating unit from 1,6-heptadiene shows glass transition temperature at − 27 to 3.2 °C, whereas those rich in ethylene unit shows melting point at 109–116 °C. In contrast, the product of the Fe complex-catalyzed reaction of ethylene and 1,6-heptadiene is a mixture of homopolymers of both monomers.

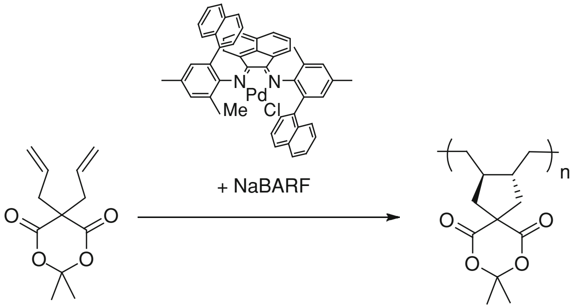
Ni diimine complex (**1b**), on the other hand, catalyzes cyclopolymerization of 9,9-diallylfluorene to give the polymer containing *cis*-1,3-disubstituted six-membered rings, exclusively [253]. Difference in the ring size and the stereochemistry of the cycloalkane group in the produced polymer obtained by the different catalysts is accounted for by the intermolecular insertion mode of C=C double bond



Scheme 4.14 Mechanism of cyclopolymerization of 1,6-heptadienes

of the diene monomer and the rate of intramolecular insertion of C=C double bond of the intermediate (Scheme 4.14).

Pd catalyst **1e**/NaBARF is effective for cyclopolymerization of 1,6-heptadienes with functional groups at 4-position, giving the polymer with *trans*-1,2-disubstituted cyclopentane group. Varieties of functional groups such as ester, acetal, imide and amide groups can be incorporated to the polymer [254]. C_2 symmetric Pd complex promotes isotactic polymerization of the dienes to afford the polymer with threo-diisotactic structure ($rr = 83\ \%$) (Eq. 4.10). Copolymerization of these monomers with ethylene and α-olefins can be achieved.



(4.10)

The reaction of Pd complex with 1,6-heptadiene affords one-to-one reaction product (Fig. 4.2) [255]. The complex promotes polymerization of diene as well as α-olefins. The polymerization of 1-hexene by the complex at −20 °C proceeds in living fashion, affording polymer with the functional group at the initiating end, and with narrow molecular weight distribution. By using functionalized olefin as a terminating agent, the polymer with functional groups on both terminal ends can be synthesized. The telechelic polymer with barbiturate group shows thermoreversible gelation properties.

Pd-catalyzed polymerization of 1,6-heptadiene having alkyl group on 7-position is accompanied by chain walking reaction to give the polymer containing both cyclopentane and oligomethylene groups in alternating sequence [256]. The intervals between neighboring cyclopentane groups can be controlled by the length of alkyl group of the monomer. Polymerization of dienes with branched alkyl chain leads to polymer having the branches in regio-selective manner [257].

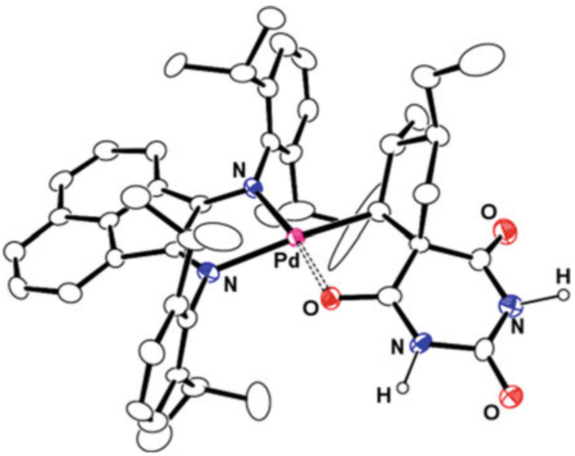
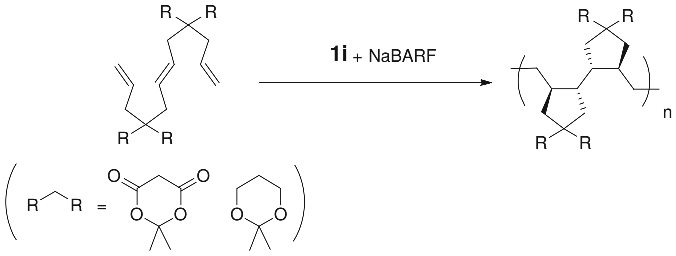


Fig. 4.2 Cyclopentyl Pd complex formed by one-to-one reaction of cationic Pd diimine complex and 5,5-diallylbartituric acid

Not only dienes, but also trienes undergo smooth polymerization, accompanying selective reaction of the three C = C double bonds of the monomer (Eq. 4.11) [258].



(4.11)

The cyclization occurs quantitatively. The polymer, thus formed by double-cyclopolymerization, has two trans-fused five-membered rings in every repeating unit. The relative stereochemistry of the two cyclopentane rings is also controlled in racemo configuration.

4.9 Summary

In these two decades, late transition metal catalyzed olefin polymerization has progressed significantly. Some features of the polymerization that are hardly observed in conventional early-transition metal catalyzed polymerization include formation of branched polymer in ethylene polymerization, copolymerization of olefin with polar monomers, and olefin polymerization in aqueous media.

Although examples of stereoselective olefin polymerization by late transition metals are limited, recent studies revealed that they promote polymerization of non-conjugated dienes and cycloolefins in high stereoselectivity. However, there are still several drawbacks in late transition metal catalysts when compared to early transition metals, such as generally low catalytic activity especially in propylene and α-olefin polymerization. The further design of new catalysts will not only solve such problems, but also explore new research areas in olefin polymerization.

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Chapter 5
Oligomerization of Olefins

Daisuke Takeuchi and Kohtaro Osakada

Abstract This article reviews recent studies on oligomerization of olefins catalyzed by transition metal complexes. Ni, Pd, and Fe complexes, having a ligand with a similar structure to the ethylene polymerization catalyst but with less bulky substituents, convert ethylene to the oligomers as a mixture with various chain lengths with Schulz–Flory molecular weight distribution. Cossee-type insertion of ethylene into the M–C bond and frequent elimination of α-olefins are proposed as the major reaction mechanism. The reaction using the Fe catalyst for polymerization and large excess of chain transfer reagents such as $ZnEt_2$ can yield the oligomers with Poisson distribution. Cr complexes with various ligands promote selective trimerization and/or tetramerization of ethylene to produce 1-hexene and/or 1-octene. The mechanism involving metallacycle is proposed to account for the selectivity. Several Ti and Ta complexes are also effective for the trimerization of ethylene. Oligomerization of α-olefins has been also studied, although the product is frequently composed of branched oligomers and/or inner olefins.

5.1 Introduction

α-Olefins, with a C=C terminal double bond ($CH{=}CH_2$ group), are extensively used as the starting materials for organic and polymer compounds. For example, α-olefins with C4–C8 are used as the comonomer for polyolefins, C10 is for lubricants, and C12–C16 are for surfactants. The α-olefins had been synthesized by Fischer-Tropsch synthesis or cracking of paraffin waxes. Oligomerization of

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olefins is more recent approach for α-olefins, which has become common and important in these several decades [1–12]. It is worth noting that the olefin oligomerization has advantage in atom economy, low energy cost, and production of the oligomer with even number of the carbon chain. Ethylene oligomerization catalyzed by Ni catalysts has been the most important oligomerization as the industrialized process [1, 2, 5]. The reaction occurs smoothly under mild conditions, but yields a mixture of ethylene oligomers with varied chain lengths. Studies on new catalysts enabled selective oligomerization of ethylene and olefins. This chapter includes recent extension of the former as well as remarkable progress of the latter.

5.2 Oligomerization of Ethylene

5.2.1 General Aspect

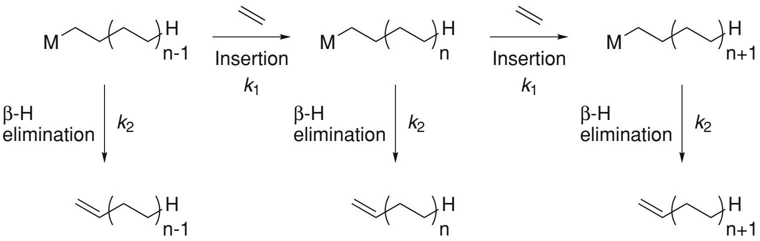
Metal-catalyzed polymerization and oligomerization of ethylene are generally composed of four reactions, Initiation, Propagation, Termination, and Chain transfer. Scheme 5.1 summarizes a series of the fundamental reactions. k_1 and k_2 stand for the kinetic constants of propagation and of termination and/or chain transfer reaction, respectively. The chain length of the product is dependent on the relative ratio between k_1 and k_2. The insertion rate k_1[ethylene], being much larger than k_2, produces high molecular weight polymer. In contrast, if k_1[ethylene] is comparable to k_2, the dimer should be formed as the major product. The competing rates of insertion and β-hydrogen elimination produce a mixture of oligoethylenes with various lengths. Distribution of the chain length of the formed oligoethylenes mostly obeys the following equation (Schulz–Flory distribution) [13, 14].

$W_m =$ $m\,\alpha^{m-1}(1-\alpha)^2$
$W_m =$ weight fraction of m mer of oligoethylene
α = rate of propagation/(rate of propagation + rate of chain transfer)
$k_1/(k_1 + k_2)$

The value α is frequently used to evaluate the product with Schulz–Flory distribution, and is obtained empirically from slope of the plot of $\log(W_m/m)$ versus m [15, 16]. For example, dimer is preferentially formed when α is close to zero. The following values β and K are also used for evaluation of the reaction.

$$\beta = \text{rate of chain transfer/rate of propagation} = (1-\alpha)/\alpha = k_2/(k_1 + k_2)$$

$$K = \text{mol fraction } C_{n+2} \text{ olefin/mol fraction } C_n \text{ olefin (chain growth factor)}$$



Scheme 5.1 Fundamental reactions in ethylene oligomerization

5.2.2 Ethylene Oligomerization to Olefins with Schulz–Flory Distribution and Dimerization

Earlier works on ethylene oligomerization have been reviewed by Skupińska [1]. Ziegler–Natta type catalysts (Ti, Zr) and Ni-based catalysts were extensively used for the oligomerization because of their high activity and selectivity. Especially, Ni ylide complex (Chart 5.1 **1a**) is highly active for oligomerization of ethylene and applied industrially to Shell Higher Olefin Process (SHOP). Recently, Matt et al. conducted the oligomerization using the ligand with electron-withdrawing COOEt and CF_3 groups at the coordinating phosphorus atom, and observed increase of the catalytic activity and shift of the products to lower molecular weight oligomer [17]. Phenacyl(diaryl)phosphine, a neutral *P*,*O*-chelating ligand, forms cationic Ni complex **1b**, which catalyzes ethylene dimerization to 1-butene (TOF: 1.3×10^6mol (mol cat.)$^{-1}$ h^{-1}) [18]. Zwitter ionic Ni complex with phosphine carboxylate ligand bonded to $B(C_6F_5)_3$ (**1c**) also functions as the catalyst for ethylene oligomerization [19].

Diimine Ni and Pd catalysts with bulky *N*-aryl groups catalyze ethylene polymerization (Chap. 4). The ortho-substituents of the aryl groups prevent chain transfer reaction and produce high mass polymer. In contrast, the complexes with less hindered *N*-aryl groups tend to afford ethylene oligomers. Ni-diimine complexes having *N*-aryl groups without *ortho*-substituents (Chart 5.1 **1d**, **1e**) afford linear α-olefins rather than polyethylene in the presence of MAO cocatalyst [20, 21]. Molecular weight distribution of the products obeys Schulz–Flory rule ($\alpha = 0.59 - 0.81$). TOF reaches up to 136×10^3 mol (mol cat.)$^{-1}$ h^{-1} and the selectivity for α-olefin is high (up to 96 %) (Table 5.1, runs 1–5). Pd and Ni complexes with bipyrazolyl ligand [22, 23] as well as unsymmetrical bidentate *N,N*-ligands such as pyridylimine ligand (**1f**) [24] and pyridine- and imidazole-phosphinimine ligands (**1g**) [25] catalyze oligomerization of ethylene to afford its dimer and/or trimer. In addition to the *N,N*-ligands, Pd and/or Ni complexes with *P,N*-ligands (**1h**–**1j**) [26–31] are used for the dimerization and oligomerization of ethylene. Brookhart prepared the Pd complex with *P,N*-chelating ligand with an eight-membered chelate ring (**1k**), and found its C–H… Pd agnostic interaction in the molecular structure and catalytic activity for ethylene oligomerization [32].

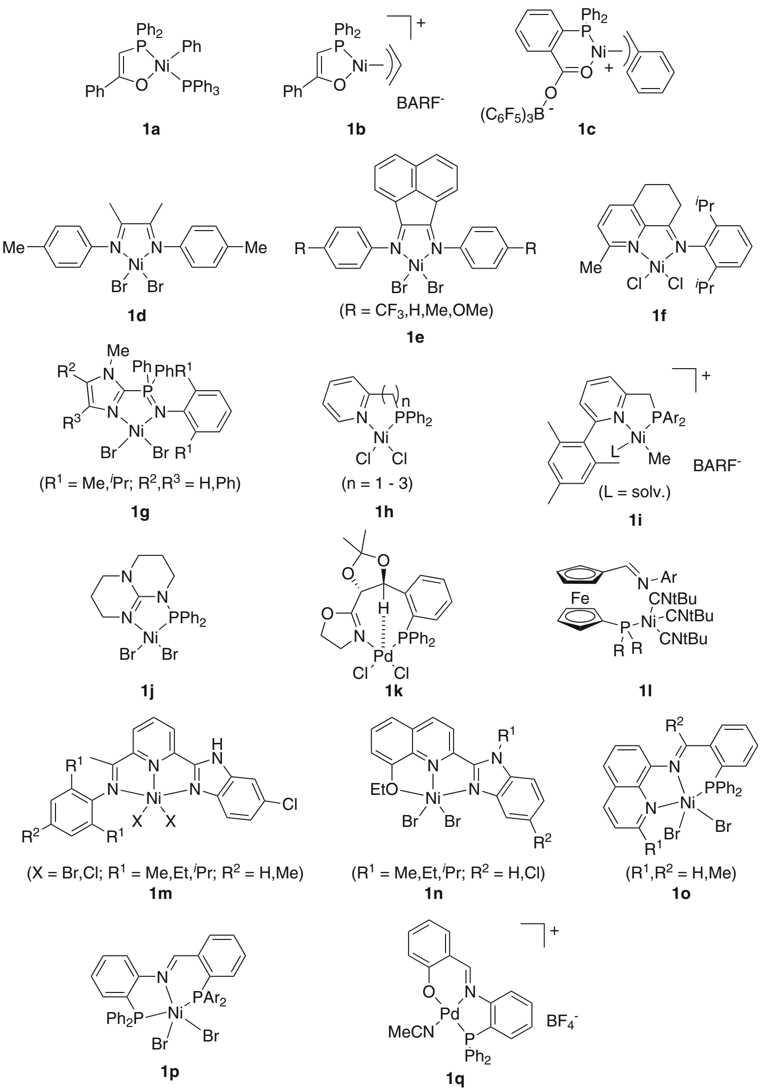


Chart 5.1 Representative Ni and Pd catalysts for ethylene oligomerization

Braunstein reported his comprehensive studies on the ethylene oligomerization catalyzed by the Ni complexes with the *P–N* ligands [3, 33–38]. Phosphinopyridine or phosphinooxazoline ligands show high activity for oligomerization of ethylene (3,300–29,100 g (g Ni)$^{-1}$ h^{-1}, TOF = 7,000–63,600 mol (mol Ni)$^{-1}$ h^{-1}) [3, 32–38]. Both the mononuclear and dinuclear Ni(II) complexes with the phosphinooxazoline ligands catalyze ethylene oligomerization with TOF of

Table 5.1 Ethylene oligomerization to olefins with Schulz–Flory distribution

Run	cat.	cocat.	Pressure/atm	Temperature/°C	Time/min	TON/mol (mol cat.)$^{-1}$	α-Olefin %	S–F α	References
1.	**1b** R = CF_3	MMAO	28	35	60	136,000	87	0.61	[20]
2.	**1b** R = Me	MMAO	56	35	60	45,000	91	0.71	[20]
3.	**1b** R = H	MMAO	28	35	60	114,000	88	0.67	[20]
4.	**1b** R = CF_3	MAO-IP	28	35	30	23,000	96	0.67	[20]
5.	**1b** R = CF_3	Et_2AlCl	28	35	30	51,000	90	0.81	[20]
6.	**1d** R = H	$EtAlCl_2$	56	55	60	63,600	85	0.59	[21]
7.	$NiBr_2(bpy)$	$EtAlCl_2$	56	55	60	61,000[a]	64	0.58	[21]
8.	**1f**	MMAO	10	20	30	45,900[a]	90	0.11	[24]
9.	**1f**	$Et_3Al_2Cl_3$	10	20	30	7,900[a]	90	0.11	[24]
10.	**2a** R = Me, M = Fe	MMAO	1	25	180	10,000[a]	>99	0.81	[48]
11.	**2a** R = Me, M = Fe	MMAO	27.2	60	30	2530,000[a]	>99	0.73	[48]
12.	**2a** R = Me, M = Fe	MMAO	40.8	90	30	17,700,000[a]	>99	0.70	[48]
13.	**2a** R = Et, M = Fe	MMAO	27.2	60	30	1,970,000[a]	>99	0.79	[48]
14.	**2a** R = ^{i}Pr, M = Fe	MMAO	1	25	60	8,000[a]	>99	0.87	[48]
15.	**2a** R = Me, M = Fe	MAO	4.93	50	60	1,300[b]	–	0.79	[49]
16.	**2a** R = Me, M = Co	MAO	9.87	50	60	50[b]	–	0.66	[49]
17.	**2a** R = Cl, M = Fe	MMAO	10	40	60	25.3[c]	>98	0.70	[50]
18.	**2b** R = cyclohexyl	MAO	4.05	25	15	60,000	–	0.74	[54]
19.	**2b** R = 1-PhEt	MAO	4.05	25	15	130,000	–	0.89	[54]
20.	**2c** R = Et	MAO	10	40	60	49.1[c]	>96	0.64	[55]
21.	**2d** R = ^{i}Pr	MAO	10	20	60	1.16[c]	>98	0.58	[56]
22.	**2j** X = 4-^{t}BuPhS $R^1 = R^2$ = Me	MMAO	68.0	50	60	91,600[d]	–	0.72 (C12/C10)	[58]

(continued)

Table 5.1 (continued)

Run	cat.	cocat.	Pressure/atm	Temperature/°C	Time/min	TON/mol (mol cat.)$^{-1}$	α-Olefin %	S–F α	References
23.	**2j** X = Ph_2P R^1 = ^{i}Pr, R^2 = H	MMAO	68.0	50	60	70,600[d]	–	0.60 (C12/C10)	[62]
24.	**3e** X = O R^1 = H, R^2 = ^{t}Bu	MMAO	10	60	30	7,360	>94	0.60	[70]
25.	**3f** R = 2,6-$^i Pr_2C_6H_3$	MMAO	1	46	30	5,490[b]	89	0.78	[71]
26.	**3f** R = 1-adamantyl	MMAO	1	25	30	40,440[b]	86	0.80	[71]

[a] TOF (mol ethylene) (mol cat.)$^{-1}$ h^{-1}

[b] g (mmol cat.)$^{-1}$ h^{-1} bar^{-1}

[c] 10^6 g (mol cat.)$^{-1}$ h^{-1}

[d] g (mmol cat.)$^{-1}$

36,300–61,000 mol (mol Ni)$^{-1}$ h^{-1}) [35–38]. The phosphinopyridine ligand with bulky substituent of the pyridine ring (ligand of complex **1i**) gives the mononuclear Ni complex, which show high catalytic activity (TOF = 61,000 mol (mol Ni)$^{-1}$ h^{-1}) [34]. The major products are butenes (56–100 %) and hexenes (up to 41 %), and the selectivity for 1-butene is rather low (up to 39 %). Formation of the byproducts other than α-olefins are explained by (1) β-H elimination after ethylene insertion, followed by reinsertion with the opposite regiochemistry and by (2) a re-uptake mechanism for isomerization of 1- to 2-butene. Although most of the Pd and Ni catalysts for the oligomerization have divalent metal center, Hor and Braunstein reported Ni(0) complex **1 l** effective for ethylene oligomerization [39].

Ni and Pd catalysts with tridentate ligands were also studied. Sun designed *N,N,N*-(**1m** and 2-imino-1,10-phenanthroline) [40–42], *N,N,O*-(**1n**) [43], *P,N,N*-(**1o**) [44], and *P,N,P*-(**1p**) [44] ligands for the Ni catalyst of ethylene oligomerization, while Liu reported structure of a cationic Pd catalyst having *P,N,O*-tridentate ligand (**1q**) [45]. The Ni complexes are activated by Et_2AlCl, $Et_3Al_2Cl_3$, and MAO, and catalyze conversion of ethylene into butene with C4 selectivity of 80–98 %. The Pd catalyst **1q** provides higher α-olefins (C6–C16) as the product of ethylene oligomerization.

The bidentate *N,N*- and *P,N*-ligands form the catalyst of not only Ni and Pd but also Co and Fe to promote the ethylene oligomerization [46–48]. Fe and Co complexes with symmetrical and bulky bis(imino)pyridine ligand show high catalytic activity for ethylene polymerization to afford linear polyethylene [4]. Similar complexes having an *ortho*-substituent for each *N*-aryl group (Chart 5.2 **2a**) are effective for ethylene oligomerization to give the oligomer with Schulz–Flory distribution ($\alpha = 0.70 - 0.87$). Activity is high as shown in Table 5.1, runs 10–17 (TOF up to 177 × 10^6 mol (mol cat)$^{-1}$ h^{-1}) [49–52]. The catalyst with unsymmetrically substituted bis(imino)pyridine ligand (**2b**) also enhances the ethylene oligomerization [53, 54].

Chart 5.2 summarizes Fe and Co complexes with unsymmetrical tridentate ligands. The complexes with varieties of *N, N, N*-(**2c**) [40, 55], (**2d**) [47, 56], (**2e**) [57], (**2f**) [58], (**2g**) [59], (**2h**) [60], and (**2i**) [61], were reported to catalyze the reaction. The *N, N, S*-, and *N, N, P*-tridentate ligands (**2j**) [62, 63], containing the diimine framework and *P*- or *S*-pendant, tend to bring about dimerization of ethylene. Typical results are summarized in Table 5.1, run 18–23. Especially, most Co complexes are effective for synthesis of 1-butene from ethylene. In contrast, the selectivity for 1-butene in C4 product is lower than the Ni-catalyzed reaction. The Fe catalysts often give longer oligomers with Schulz–Flory chain length distribution.

In addition to the late transition metal complexes, Cr complexes with meridional tridentate ligands promote ethylene oligomerization. Chart 5.3 summarizes the complex with the tridentate ligand, **3a** [64], **3b** [65], **3c** [66], **3d** [67–69], and **3e** [70] (Table 5.1 run 24). Most of the complexes afford oligomers with Schulz–Flory distribution. Depending on the substituents of the ligand, the catalyst changes the product from the oligomer to polyethylene. Recently, Cr complex **3f** with the tridentate ligand having two *N*-heterocyclic carbene sites was found to be

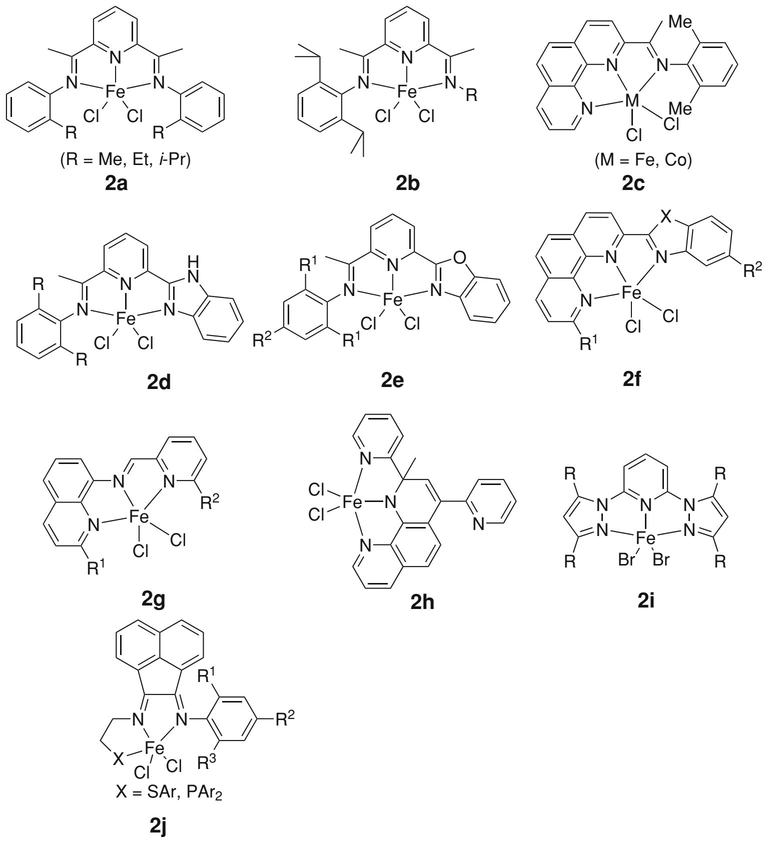


Chart 5.2 Fe and Co catalysts for dimerization and oligomerization of ethylene

very active for ethylene oligomerization (up to 40,440 g (mmol Cr)$^{-1}$ h^{-1} bar^{-1}) (Table 5.1, runs 25, 26). In this case, the produced oligomer again obeys Schulz–Flory distribution ($\alpha = 0.46 - 0.80$) [71–73]. Cr complex with phenoxy imine ligands having a pyridyl pendant at the imine nitrogen catalyzes ethylene oligomerization [74].

5.2.3 Ethylene Oligomerization to α-Olefins with Poisson Distribution

Oligomerization of ethylene giving the product with Poisson distribution was also reported. Gibson found that ethylene oligomerization catalyzed by bis(imino)pyridine iron complex in combination with MAO and $ZnEt_2$ is accompanied by rapid transmetalation between alkyliron and dialkylzinc compounds. Chain growth

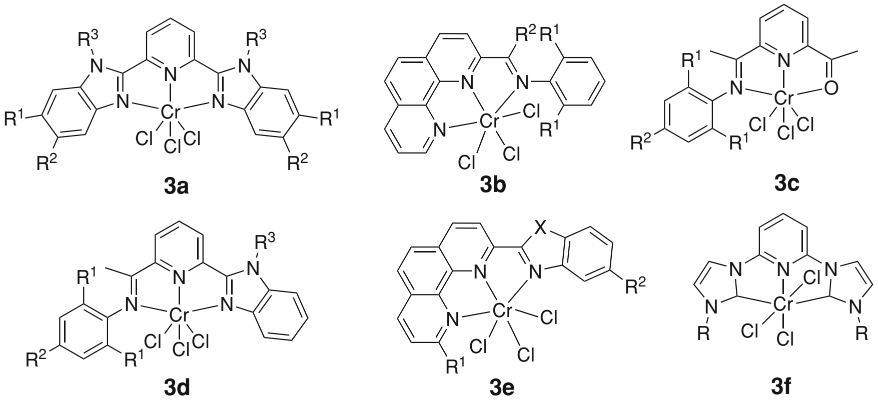


Chart 5.3 Representative Cr catalysts for ethylene oligomerization

occurs at the Fe center, and ceases after transfer of the alkyl ligand to Zn. The treatment of the resulting growing species with Ni(acac)$_2$ results in further transmetalation to Ni followed by β-hydrogen elimination of linear α-olefin (Scheme 5.2). The chain growth takes place in living fashion, and the produced α-olefin has Poisson distribution [75].

Hessen reported that divalent half-zirconocene alkyl complex promotes oligomerization of ethylene in the presence of 1-pentene at 20 °C [76]. Warming the reaction mixture at 50 °C leads to chain transfer of the growing species to 1-pentene to give α-olefins (both even and odd carbon numbers) with Poisson distribution.

Many other Ti and Zr complexes also show high catalytic activity for ethylene oligomerization, but they have tendency to form polyethylene and branched oligomers.

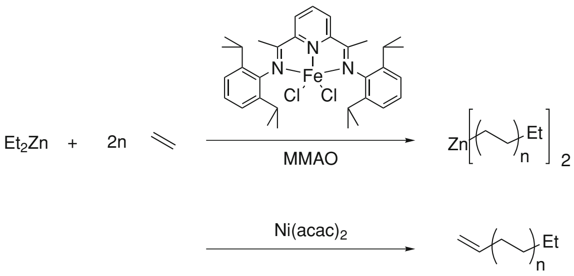
5.3 Selective Trimerization of Ethylene

As mentioned above, most of the transition metal catalysts promote the ethylene oligomerization via Cossee mechanism, to yield the products with Schulz–Flory chain length distribution. In contrast, Cr catalysts with some specific ligands have been found to promote selective trimerization and tetramerization of ethylene [2, 6, 8, 10, 11], while Ti and Ta catalysts are active for the trimerization are also known [2, 12]. Those reactions proceed via a metallacycle mechanism.

5.3.1 Chromium Catalyst

In 1967, researchers of Union Carbide Corporation found formation of 1-hexene as a predominant product during their studies of ethylene polymerization catalyzed

Scheme 5.2 Fe-Catalyzed ethylene oligomerization to α-olefins with Poisson Destribution

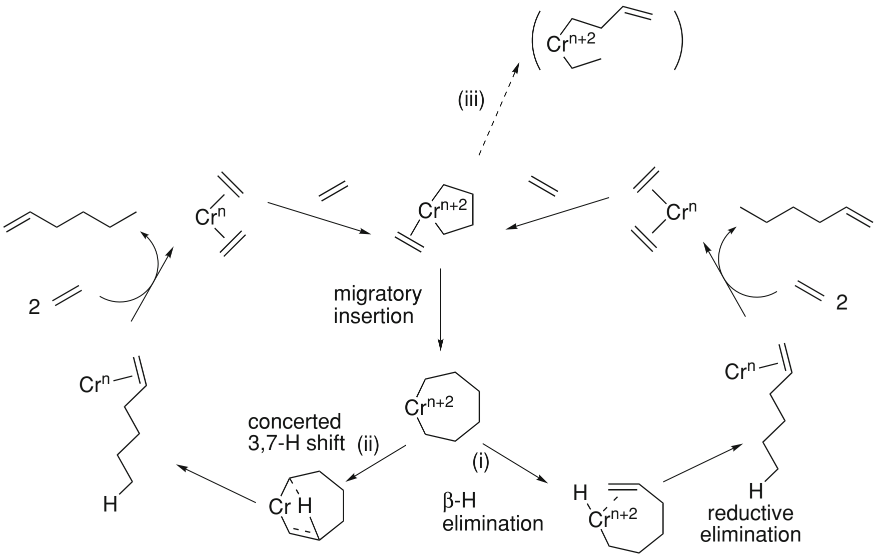


by Cr(III)-tris-2-ethylhexanoate in combination with hydrolyzed ^{i}Bu$_3$Al cocatalyst [2]. Later, addition of dimethoxyethane to the catalyst system was found to improve the selectivity to 74 % [77, 78]. Pyrrolyl-Cr complexes also catalyze the ethylene trimerization. A number of modified Cr catalysts for ethylene trimerization were registered in their patents.

Selective formation of 1-hexene suggested a reaction mechanism distinct from the Ni, Fe, and Co catalysis, which involves Cossee-type insertion of ethylene into a metal-alkyl bond and β-hydrogen elimination and produces an oligomer mixture with a statistical distribution of the molecular lengths. Scheme 5.3 shows the proposed mechanism for the ethylene trimerization.

Oxidative coupling of ethylene on the Cr center forms chromacyclopentane. Coordination of a new ethylene molecule, and its insertion into a Cr–C bond results in formation of chromacycloheptane. A seven-membered cyclic product is kinetically less stable than the chromocyclopentane and releases the product with regeneration of low valent Cr species with π-coordinated ethylene molecules. Although these reactions would rationalize formation of 1-hexene, there may have multiple possibilities for release of 1-hexene from the metallacycle intermediate. One involves β-hydrogen elimination, forming 5-hexenyl chromium complex and reductive elimination of 1-hexene (Scheme 5.3i). A non-classic mechanism, involving 3,7-hydrogen shift of the chromacycloheptane, is also proposed for elimination of the olefin product (Scheme 5.3ii). β-Hydrogen transfer from the metallacycle to coordinated monomer would lead to reductive elimination of 1-hexene (Scheme 5.3iii), although this pathway is not discussed in most of the reports. A chromacycloheptane has been synthesized by the reaction of Cr(III) complex with 1,6-hexadienyl dimagnesium chloride, and it decomposes instantly to release 1-hexene [79].

Theoretical studies on ethylene trimerization by Cr-pyrrolyl complex and bare Cr complex have been reported [80]. DFT calculation on the Cr-pyrrolyl complexes concluded that metallacycle pathway is energetically favored and involves ring expansion as the rate-determining step. The pyrrole ligand changes its bonding mode between η^5- and σ-ones during the reactions. Thus, the ring slippage of the pyrrole renders the reaction smooth. Cossee and the metallacycle mechanisms on chlorinated Cr-based catalysts are compared by DFT calculations



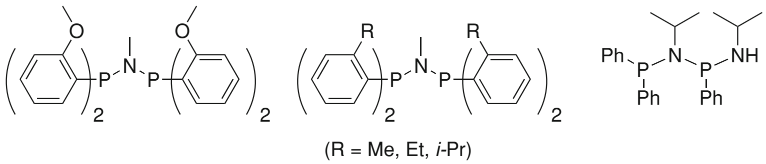
Scheme 5.3 Proposed mechanism for the ethylene trimerization

[81]. The latter pathway with cationic Cr(II)–Cr(IV) intermediates is the most favored, where the rate-determining step resides in the oxidative coupling of two coordinated ethylene to form the chromacyclopentane.

5.3.1.1 Chromium Catalyst with PNP Ligands

A mixture of $CrCl_3(thf)_3$ and bis(diarylphosphino)amine, $RN\{P(C_6H_4\text{–}o\text{–}OMe)_2\}_2$ (Chart 5.4 **4a**), catalyzes trimerization of ethylene in the presence of MAO. Activity over 1 million g (g Cr)$^{-1}$ h^{-1} is observed (20 bar ethylene, Table 5.2, runs 1, 2) [82]. The reaction system is thermally robust enough to be active even at 110 °C. The selectivity of 1-hexene is typically over 85 %. The *ortho*-OMe group may act as pendant donors, occupy the coordinatively vacant site of the chromium center, and stabilize the catalyst. The ligands with *o*-OEt and *p*-OMe substituents of the *P*-aryl groups and dppm backbone instead of **4a** do not form the active catalyst.

A mixture of $CrCl_3(thf)_3$ or $Cr(acac)_3$ and bis(diarylphosphino)amine ligands with 2-alkylphenyl groups at the phosphorus atoms (Chart 5.4 **4b**) catalyzes ethylene oligomerization to form the trimers and a smaller amount of tetramers as the major products [83]. The ligands having *ortho*-methyl- and ethylphenyl groups on the P atoms lead to the preferred formation of C6 products (86–93 %) (1-hexene/C-6 products >99.1 %), the activity ranging from 100,840 to 324,110 g (g Cr)$^{-1}$ h^{-1} (Table 5.2, runs 3–6). Decreasing the number of *ortho*-substituents on the aryl groups lowers 1-hexene selectivity and enhances 1-octene formation.



4a **4b** **4c**

Chart 5.4 Representative PNP ligands for Cr catalysts of ethylene trimerization

Use of bis(diphenylphosphino)amine without ortho substituents forms a mixture of C6 (41.5 % yield) and C8 (41.9 % yield). The catalyst having the ligand with two *ortho*-methyl substituents, both symmetrical and unsymmetrical ones, results in increased formation of 1-octene. In contrast, changing the *N*-methyl group with *N*-isopropyl group leads to increased formation of C6 product.

Agapie and Bercaw synthesized and isolated triphenyl Cr complex and biphenylene Cr complex with the bis(diarylphosphino)amine ligand (Chart 5.5 **5a**, **5b**) [84–87]. X-ray crystallography of the latter complex suggested P–O chelating coordination of a *P*-aryl group. The triphenyl Cr complex **5a** reacts with ethylene to yield styrene and ethylbenzene rather than 1-hexene. Activation of it with $H(Et_2O)_2BARF$ (BARF = $B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$), however, provides the catalyst for 1-hexene formation with a similar activity to a mixture of $CrCl_3$-**4a** [82]. Cr complex **5b** also promotes the trimerization in the presence of NaBARF. Thus, the catalytic trimerization catalyzed by a mixture of Cr salt, **4a**, and MAO involves a cationic Cr complex as the active species. Trimerization of an equimolar mixture of C_2H_4 and C_2D_4 catalyzed by **5a**/$H(Et_2O)_2BARF$ or **5b**/NaBARF affords only four isotopomers C_6D_{12}, $C_6D_8H_4$, $C_6D_4H_8$, and C_6H_{12} in a 1:3:3:1 ratio (Scheme 5.4i). The reaction proceeds via a metallacycle route rather than via repetition of Cossee-type insertion and β-hydrogen elimination, because isotopomers containing an odd number of deuterium due to H/D scrambling are not found in the reaction mixture. The reaction of *cis*-1,2-dideuterioethylene by **5b**/NaBARF gives a mixture of two isotopomers with CHD=CH- and CDH=CD- fragments in 1:2.4 ratio and no H/D scrambled isotopomers having a CH_2= or CD_2= group (Scheme 5.4ii). The 1,1-dideuterioethylene also produces four isotopomers shown in Scheme 5.4iii, selectively.

All these results suggest intermediacy of the chromacycloheptane in the ethylene trimerization. Kinetic isotope effects of the reaction indicated that the rate-determining step of the reaction should involve C–H bond cleavage process such as β-hydrogen elimination from the chromacycloheptane, giving a hydride(5-hexenyl) chromium species, or 3,7-hydrogen shift of the metallacyclic intermediate.

Trichlorochromium(III) complex having ligand **4a** (Chart 5.5 **5c**) shows dynamic NMR spectra due to fluxional behavior of the ether groups interchanging on the NMR time scale [86]. Oxidation of Cr(0)-carbonyl complex **5d** (Chart 5.5) with $[AcFc]BF_4$ yields cationic Cr(I) complex, $[Cr(CO)_4($**4a**$)]BF_4$, which does not catalyze ethylene trimerization [88]. Addition of $AlEt_3$ to the cationic complex

Table 5.2 Trimerization of ethylene

Run	cat.	cocat.	Pressure/ atm	Temperature/ °C	Time/ min	Productivity/ g (gmetal)$^{-1}$ h^{-1}	α-Olefin wt%	C6 wt%	C8 wt%	References
1.	$CrCl_3(thf)_3$/**4a**	MAO	2	80	60	4,610	99.7	91.5	0.6	[82]
2.	$CrCl_3(thf)_3$/**4a**	MAO	20	80	60	1,033,200	99.9	90.0	1.8	[82]
3.	$Cr(acac)_3$/**4b** R = Me	MMAO	44.4	45	13	298,800	99.1	86.0	10.5	[83]
4.	$Cr(acac)_3$/**4b** R = Et	MMAO	44.4	45	10	324,110	99.7	90.7	4.2	[83]
5.	$CrCl_3(thf)_3$/**4b** R = Et	MMAO	44.4	45	15	161,660	99.8	93.0	3.6	[83]
6.	$Cr(acac)_3$/**4b** R = ^{i}Pr	MMAO	44.4	45	20	100,840	99.3	92.9	2.7	[83]
7.	**5e**	Et_3Al	29.6	65	120	289	98	86	2	[89]
8.	$Cr(acac)_3$/**4c**	Et_3Al Et_4PCl	29.6	50	60	26,700	99.0	93.0	0.3	[91]
9.	**5f** R = ^{i}Pr	MAO	29.6	45	30	4,579	95	97	1	[92]
10.	**5f** R = Ph	MAO	29.6	70	30	9,783	98	99	1	[92]
11.	$CrCl_3$(**6a**) R = Et	MAO	39.5	100	30	69,340^a	99.1	94	–	[93]
12.	$CrCl_3$(**6a**) R = Ph	MAO	39.5	100	30	17,620^a	99.1	83	–	[93]
13.	$CrCl_3$(**6b**) R = Et	MAO	29.6	80	30	160,840	98.4	99.7	–	[94]
14.	$CrCl_3$(**6d**)	MAO	39.5	100	30	14,770	97.9	81	–	[80]
15.	$CrCl_3$(**6e**) E = PPh_2	MAO	29.6	24–30	60	5,742^a	99	82	–	[100]
16.	$CrCl_3$(**6e**) E = SEt	MAO	29.6	24–30	60	2,294^a	98	83	–	[100]
17.	**7a**	MAO	29.6	80	30	32,400	98.4	97.6	1.3	[102]
18.	**7b**	MAO	29.6	80	30	53,000	99.1	98.5	1.4	[102]
19.	**7c**	MAO	29.6	80	30	38,200	99.3	97.8	1.1	[102]
20.	**7d** E = NH	MAO	29.6	80	30	10,500	98.7	92.1	3.5	[102]

(continued)

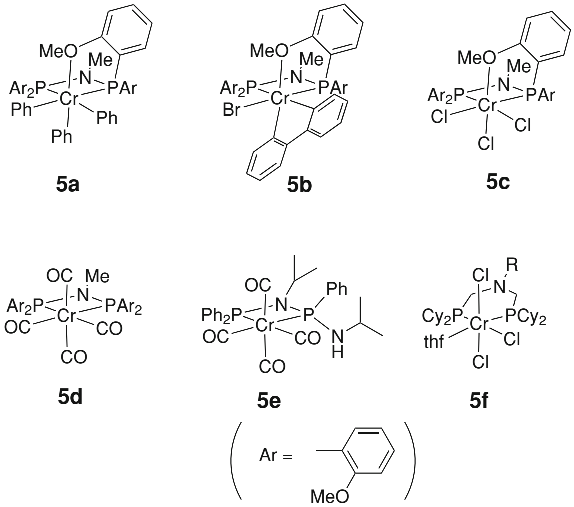
Table 5.2 (continued)

Run	cat.	cocat.	Pressure/ atm	Temperature/ °C	Time/ min	Productivity/ g (gmetal)$^{-1}$ h^{-1}	α-Olefin wt%	C6 wt%	C8 wt%	References
21.	**8a**	MAO	9.87	30	30	6,292[b]	–	87	–	[110]
22.	**8a**	MAO	4.93	30	30	110,000[a]	–	83	–	[111]
23.	**8b**	MAO	4.93	30	30	211,000[a]	–	84	–	[110]
24.	**8c**	MAO	5	30	30	156[b]	–	84 (1-hexene)	–	[120]
25.	**8d**	MAO	49.3	30	60	6,590[b]	–	92.3	–	[122]
26.	**9a**	Me_4Sn	47.6	45	240	385[a]	–	94 (1-hexene)	–	[123]
27.	**9a**	Me_2Zn	47.6	45	240	460[a]	–	96 (1-hexene)	–	[123]
28.	**9b**	–	48	70	60	979[a]	–	98.5	–	[125]
29.	**9b**	–	48	100	240	1,008[a]	–	95.8	–	[125]

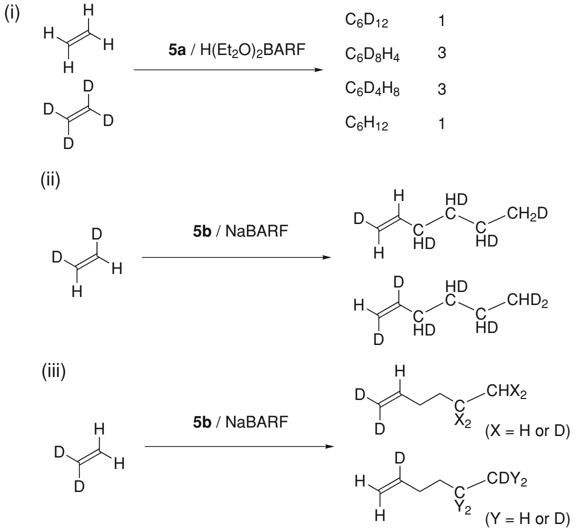
a (TOF) mol (mol cat.)$^{-1}$ h^{-1}

[b] kg (mol cat.)$^{-1}$ h^{-1}

Chart 5.5 Cr complexes used as the catalysts of ethylene trimerization



Scheme 5.4 Trimerization of deuterated ethylenes by Cr catalysts with bis(diarylphosphino)amine ligand



causes elimination of a CO ligand and starts to catalyze ethylene trimerization. The ligand with 2-(methylthio)phenyl groups prefers a SPS coordination rather than the OPP coordination.

Cr(0) complex with a PNPNH ligand (**4c**), **5e** (Chart 5.5), catalyzes ethylene trimerization in the presence of Et_3Al (activity = 289 g (g Cr)$^{-1}$ h^{-1}, C6 = 86 %, 1–C6 = 98 %) (Table 5.2, run 7) [89–91]. The reaction obeys first-order kinetics to ethylene and catalyst concentrations with the activation energy of 52.6 kJ mol^{-1} [90]. A mixture of $CrCl_3(thf)_3$ and the aluminum adduct of PNPNH (Chart 5.4 **4c**) or aluminum amide, formed by the reaction of **4c** with organoaluminum, is also active for the trimerization. Cr(acac)$_3$/**4c**/AlEt$_3$, on the other hand, does not promote the reaction, whereas addition of Et$_4$PCl makes it active for the selective ethylene trimerization (activity = 26,700 g (g Cr)$^{-1}$ h^{-1}, C6 = 93.0 %, 1–C6 = 99.0 %) (Table 5.2, run 8). Al/Cl ratios in the reaction using CrCl$_3$ as the catalyst precursor affect the catalytic activity, indicating the importance of chloride in activation of the Cr–Cl bonds.

Cr complex with a bidentate PCNCP ligand (Chart 5.5 **5f**) promotes ethylene trimerization upon activation with MAO (activity up to 9,783 g (g Cr)$^{-1}$ h^{-1}, C6 = 99 %, 1–C6 = 98 %) (Table 5.2, run 9, 10) [92]. The ligand is coordinated by the Cr center in a *P,P*-bidentate form. The reaction using the ligand with sterically bulky substituents on the P and N atoms keeps selectivity of 1-hexene, while use of less bulky substituents causes increased formation of C8 products in addition to the C6 products. DFT calculations of the intermediate indicate that formation of Cr(I)-(1-hexene) complex from chromacycloheptane complex proceeds via intramolecular 3,7-hydrogen shift and not from β-hydrogen elimination/reductive elimination.

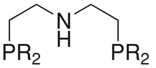
5.3.1.2 Chromium Catalyst with Tridentate PNP or SNS Ligands

Tridentate ligands listed in Chart 5.6 are used for the ligands of Cr catalyst for ethylene trimerization. Cr complex with *P,N,P*-ligand **6a** (R = Et) shows high activity and excellent selectivity for the ethylene trimerization [93]. TOF of the catalyst attains to 69,340 mol (mol Cr)$^{-1}$ h^{-1} with 99.1 % selectivity for 1-hexene (Table 5.2, runs 11, 12).

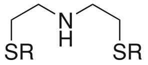
An *S,N,S*-ligand **6b** (Chart 5.6) reacts with CrCl$_3$ to form trivalent complex, CrCl$_3$(**6b**), having a meridional tridentate ligand bonded to an octahedral Cr center. The structure is similar to the tridentate PNP complex, and the chelating bite angels of the ligands, Cr–S or Cr–P distances, and Cr–N distances are almost similar between the SNS and PNP complexes. Complex of **6b** (R = Et) shows high activity (up to 160,840 g (g Cr)$^{-1}$ h^{-1}) and selectivity (98.4 % selectivity for 1-hexene and 99.7 % selectivity for C6 product) for ethylene trimerization (Table 5.2, runs 13) [94]. Cr(III) catalyst having **6b** (R = decyl) improves the catalytic activity on addition of MAO (30–100 eq to Cr), partly due to enhanced solubility of the ligand in the solvent.

Gambarotta and Duchateau chose **6b** and **6c**, having a pyridyl group as the coordinating group, as the supporting ligand of the Cr complexes and investigated details of their activation by cocatalysts. Scheme 5.5 summarizes the reaction of organoaluminum compounds with the Cr complexes having the SNS ligands.

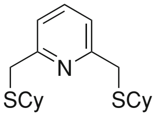
AlCl$_3$ converts CrCl$_3$(**6b**) (R = cyclohexyl) to mono- and di-nuclear cationic Cr complexes **A** and **B**, depending on the Al to Cr ratio [95]. Addition of excess Me$_3$Al (10 equiv) to a mixture of CrCl$_3$ and **6b** causes formation of a cationic dinuclear Cr complex {(**6b**)CrMe(μ-Cl)}$_2${(Me$_3$Al)$_2$(μ-Cl)}$_2$ (**C**). A similar cationic complex with ethyl ligands, {(**6b**)CrEt(μ-Cl)}$_2$-[EtAlCl$_3$]$_2$, was obtained by the reaction of CrCl$_3$(**6b**) with AlEt$_2$Cl [96]. The complex does not undergo β-hydrogen

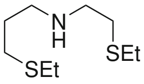

(R = Et, Ph, cyclohexyl)

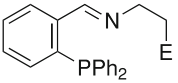
6a


(R = Me, Et, Ph, decyl)

6b


6c


6d


6e

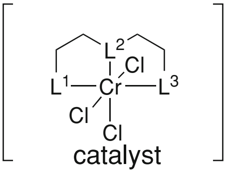
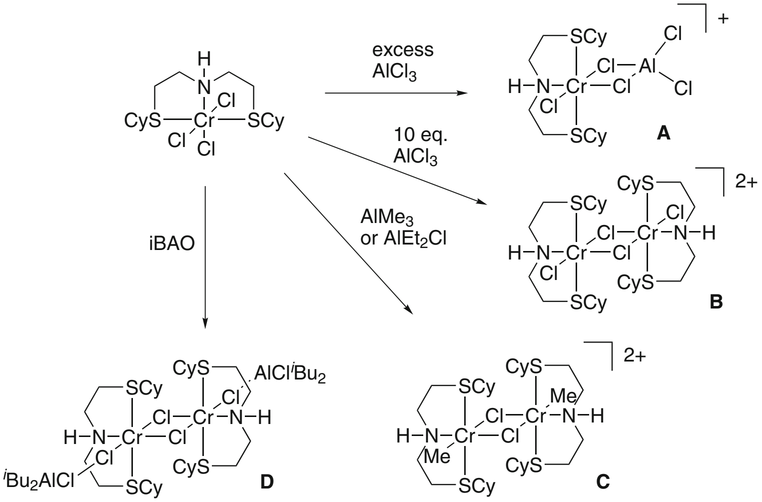


Chart 5.6 Representative tridentate ligands for Cr-catalyzed ethylene trimerization



Scheme 5.5 Reaction of Cr complex having SNS ligand with aluminum compounds

elimination from the Cr-Et group even in the presence of excess cocatalyst. By the addition of MAO, these complexes catalyze ethylene trimerization with a similar reactivity to $CrCl_3$(**6b**). The reaction of $CrCl_3$(**6b**) with isobutylaluminoxane (iBAO) leads to dinuclear divalent Cr complex (Scheme 5.5 **D**), which also acts as the selective trimerization catalyst. Thus, the trivalent Cr complex is general precursors, and yields a catalytically active divalent species in the presence of the cocatalyst. Addition of excess alkylating agents (MAO, Me_3Al, Et_3Al), however, degrade the Cr(III) complexes rapidly.

Cr(III) complexes with 2,6-bis(thiolatomethyl)pyridine (**6c**, R = Ph, Cy) also catalyze ethylene trimerization [97]. Reaction of **6c** with $CrCl_2(thf)_2$ causes formation of the Cr(II) complex. Although the Cr(III)-**6c** complex converts ethylene to

1-hexene selectively in moderate activity, $CrCl_2$(**6c**) promotes the oligomerization of ethylene to the product with a statistical distribution of molecular weights.

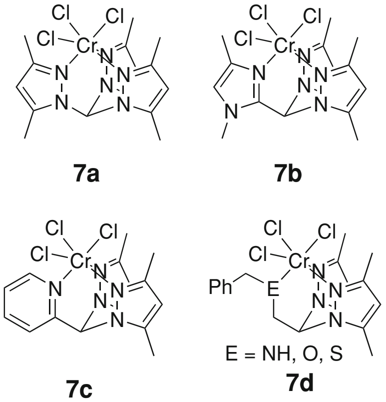
Further studies on the tridentate ligands with various substituents, donor atoms, and structures were conducted [98, 99]. Introduction of Me or benzyl substituents at N atom of the PNP ligand leads to dramatic decrease of the productivity and selectivity for 1-hexene, accompanied by increase of the polymer. The complex with the SNS ligand having a trimethylene spacer, **6d**, also catalyzes selective trimerization, but the activity and selectivity for C6 product is lower than the ligand with ethylene spacer only (activity = 14,770 (g Cr)$^{-1}$ h^{-1}, C6 = 81 %, 1–C6 = 97.9 %, Table 5.2, run 14). Cr complex with $Ph_2PCH_2CH_2SCH_2CH_2PPh_2$ (tridentate PSP) ligand does not cause selective trimerization, but produces a mixture of the oligomers with Schulz–Flory distribution. Similar PSP Cr complex with Et-P group results in predominant formation of 1-hexene, although the activity and selectivity are lower than those with PNP and SNS ligands also [99]. Cr complex with $EtSCH_2CH_2PPhCH_2CH_2SEt$ (tridentate SPS) ligand shows almost similar result to that with the PSP ligand with PEt_2 groups. McGuinness also prepared Cr(II) and Cr(III) complexes with tridentate PNP or SNS ligands. The performance of Cr(II) precatalysts is comparable with their Cr(III) counterparts on MAO activation. These ligands are easily deprotonated by added base to yield the active complexes for ethylene trimerization.

Bluhm reported the Cr complexes with PNP and SNS ligands having *ortho*-phenylene spacer between the P or S atom and N atom, and/or imine structure (Chart 5.6 **6e**) [100]. Meridional tridentate coordination of these ligands is confirmed by X-ray crystallography. The complex with PNP and PNS type ligands with imine center brings about selective formation of 1-hexene (C6 = 82–98 %) with good activity (TOF = 2,294–5,742 mol (mol Cr)$^{-1}$ h^{-1}) (Table 5.2, run 15, 16), but other complexes tend to afford polyethylene.

5.3.1.3 Chromium Catalyst with Facial Tridentate Ligands

Braunstein and Hor reported that Cr(III) complexes with heteroscorpionate pyrazolyl ligands are effective for selective trimerization of ethylene [101] (Chart 5.7). The C6 selectivity of tris(pyrazolyl)methane Cr complex (Chart 5.7 **7a**) is 97.6 wt%, and the activity is up to 32,400 g (g Cr)$^{-1}$ h^{-1} (Table 5.2, run 17) [102]. The facial tridentate coordination of the ligand is conformed by X-ray crystallography.

Cr complex with bis(pyrazolyl)(imidazolyl)methane ligand (Chart 5.7 **7b**) shows improved activity (53,000 g (g Cr)$^{-1}$ h^{-1}) retaining high selectivity (C6 = 98.5, 1–C6 = 99.1 %) (Table 5.2, run 18). Complexes **7c** and **7d** also catalyze the reaction with similar selectivity (Table 5.2, run 19, 20) [102]. Further crystallographic analysis on the intermediate formed by the reaction of the Cr complex and organoaluminum [103]. Tris(pyrazolyl)methane Cr complex (Chart 5.7 **7a**) reacted with Me_3Al (6 equiv.) and with MAO (10 equiv.) to produce the corresponding cationic dinuclear Cr(II) complex and Me_2AlX adduct of Cr(III)Cl_2Me complex (Scheme 5.6i).



7a 7b 7c 7d

Chart 5.7 Representative Cr complexes with heteroscorpionate ligands for ethylene trimerization

Further addition of 2 equiv. of Me_3Al converts the $Cr(III)Cl_2Me$ complex to the cationic Cr(II) complex. The reaction with Me_3Al-free MAO affords neither of the complexes, indicating Me_3Al is active reductant. As the cationic Cr(II) complex shows very low activity for ethylene trimerization in the presence of Me_3Al, MAO is also essential for the trimerization process. The reaction of excess Me_3Al with the bis(pyrazolyl)methane benzylamine Cr complex (Chart 5.7 **7d** (E = NH)) results in dehydrogenation from the NH and aryl CH groups of the ligand to give a heterobimetallic Cr–Al complex (Scheme 5.6ii). Thus, Me_3Al plays varied roles in the catalysis.

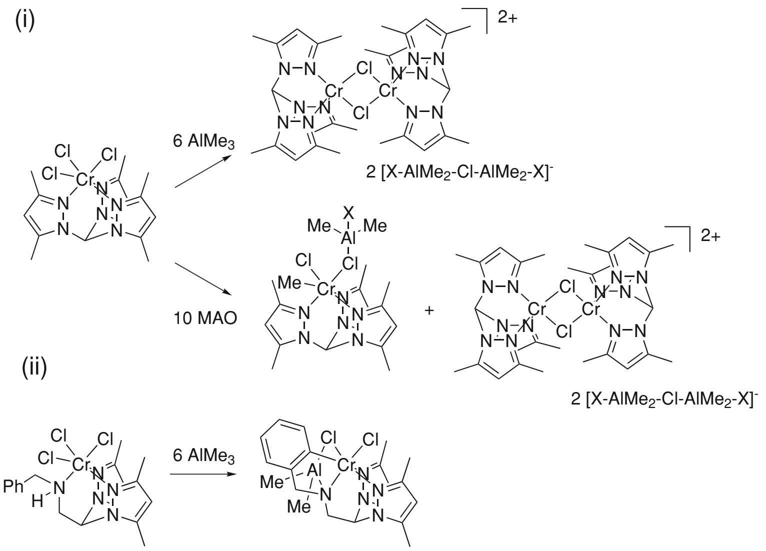
Duchateau and Mountford also studied Cr catalysts with various heteroscorpionate ligand, including bis(pyrazolyl)methane with pendant secondary and tertiary amine donors as well as phenol and phenyl ether donors [104]. Most of the complexes show improved activity compared to the complex with tris(pyrazolyl)methane ligand (up to 3,250 g (mmol Cr)$^{-1}$ h^{-1}).

5.3.1.4 Single Component Chromium Catalyst

Cr complexes with the phosphenimidous diamide ligands act as the single component catalyst for the ethylene trimerization [105, 106]. Reaction of $^{i}Bu_3Al$ with $[(^{t}Bu_2N)_2P]_2Cr$ affords complex **E** or **F** depending on the Al/Cr ratio (Scheme 5.7).

The complexes catalyzed ethylene polymerization while addition of $^{i}Bu_3Al$ cocatalyst to the reaction mixture changes the product to 1-hexene. Al–Cr heterobimetallic complex (**G**) obtained from the reaction of Me_3Al with $[(^{t}Bu_2N)_2P]_2Cr$ (4:1) (Scheme 5.7i) catalyzes the trimerization of ethylene without the cocatalyst (600 g (mmol Cr)$^{-1}$ h^{-1}, C6 = 99.9 %) [105].

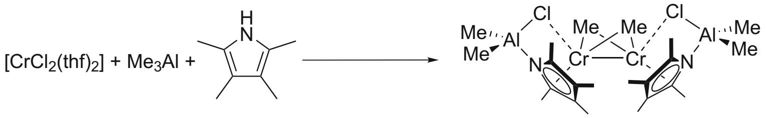
An equimolar reaction of vinylmagnesium chloride with $[NPN]CrCl_2Li(thf)_2$ affords trinuclear Cr complex (**H**) (Scheme 5.7ii) [107]. Despite apparent Cr(II)/Cr(I) mixed valence species, DFT calculations revealed that all of the Cr atoms are divalent. The complex promotes ethylene trimerization without cocatalyst (1,740 g (g Cr)$^{-1}$ h^{-1}).



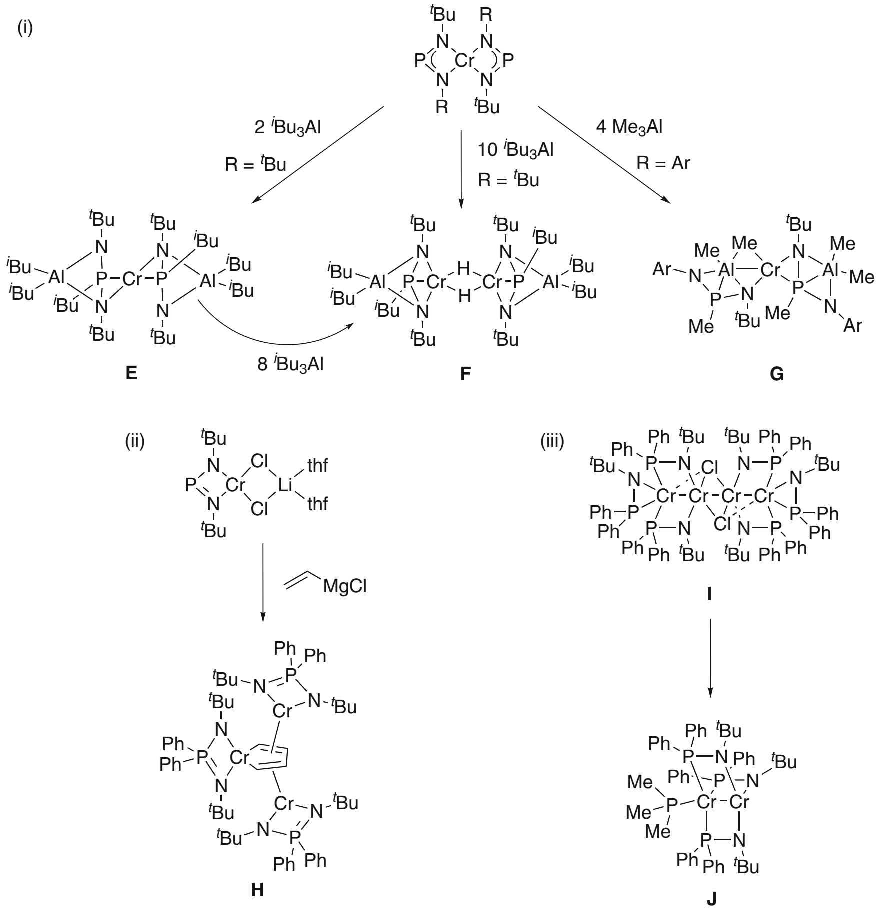
Scheme 5.6 Reaction of Cr complexes with heteroscorpionate ligands with organoaluminums. X = Cl or Me

Dinuclear mixed-valence Cr(I)/Cr(II) complex with Ph_2P-N(^{t}Bu) ligand, **J**, is obtained by the reaction of tetranuclear Cr complex **I** with PMe_3 and KC_8, and promotes oligomerization of ethylene to give a mixture of 1-butene and 1-hexene (Scheme 5.7iii) [108]. Activation of the complex with DMAO/Et_3Al cocatalyst, causes selective trimerization. In contrast, the activation with Et_3Al and with DMAO (dried MAO) results in selective dimerization and polymerization, respectively.

Dinuclear Cr complex, obtained by the reaction of $CrCl_2(thf)_2$, Me_3Al, and tetramethylpyrrole (Eq. 5.1), is also active for ethylene trimerization in methylcyclohexane in the absence of cocatalyst (activity = 670,000 g (mol Cr)$^{-1}$ h^{-1}, C6 = 95 %) [109].

 (5.1)

Use of toluene as the solvent decreases selectivity for C6 fraction (C4 = 46 %, C6 = 39 %). The Cr complex in combination with cocatalyst does not change the product selectivity significantly. The complexes obtained from $CrCl_3(thf)_3$ catalyze ethylene polymerization without a cocatalyst.



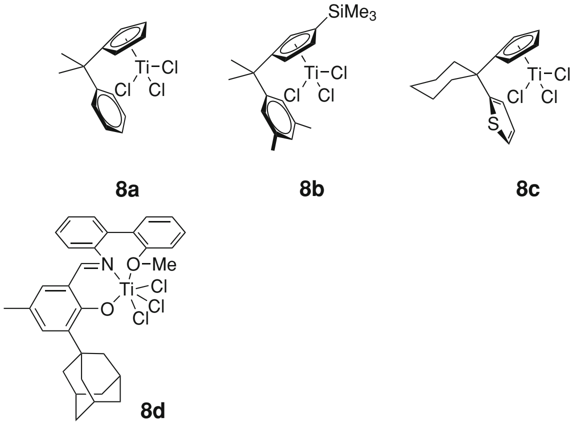
Scheme 5.7 Single component Cr catalysts formed from Cr complexes having $(R_2N)_2P$ or $(^tBu)N\text{-}PPh_2$ ligands

5.3.2 Titanium Catalyst

In 2001, Hessen reported trimerization of ethylene catalyzed by $CpCMe_2PhTiCl_3$/MAO (Chart 5.8 **8a**) with catalytic activity of 6,292 kg (mol Ti)$^{-1}$ h^{-1} (Table 5.2, run 21, 22) [110]. The reaction proceeds at 30 °C and the selectivity for 1-hexene is 83–87 wt%. C10 products (mainly 5-methylnon-1-ene, >75 %) are also formed as a result of cotrimerization of ethylene and 1-hexene (9–14 wt%). A similar Ti complex without the aryl group of the ligand affords polyethylene rather than 1-hexene.

Accompanying formation of high molecular weight polyethylene lowers yield of 1-hexene and causes reactor fouling. Detailed investigation of the reaction revealed that polyethylene is formed at early stage of the reaction, which is

Chart 5.8 Representative Ti catalyst for ethylene trimerization



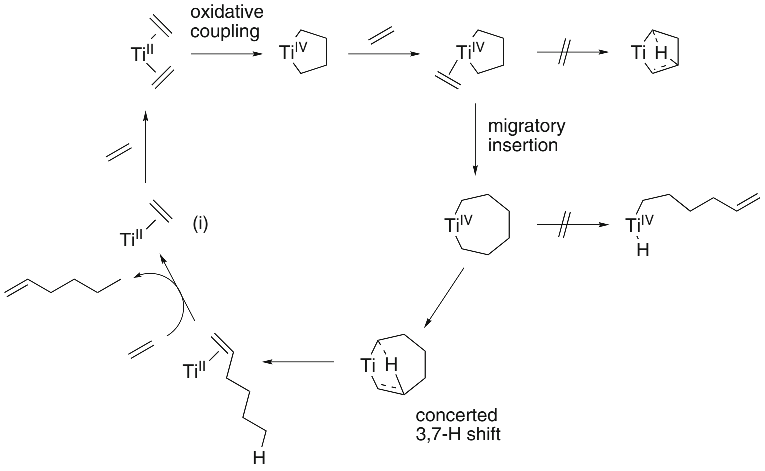
promoted by partly alkylated titanium species. The amount of produced polyethylene can be largely reduced if the complex is premixed with MAO prior to injection into the reaction mixture. Type of organoaluminum cocatalyst is also important for the reduction of polyethylene. The use of MAOs that do not contain and/or are not able to generate aluminum hydride species increases productivity of 1-hexene and depress the polyethylene formation.

Pendant aryl groups and bridging groups between the Cp and aryl groups of the ligand influence selectivity of 1-hexene [111]. The highest activity and selectivity for trimerization is obtained for the catalysts with isopropylidene-bridged 3,5-dimethylphenyl group (Table 5.2, run 23). A $SiMe_3$ substituent on the Cp ligand improves the catalyst activity and selectivity, whereas methyl substituent on the aryl group decreases activity.

Coordination of the pendant arene moiety to the titanium center is confirmed for $[CpCMe_2C_6H_3Me_2\text{-}3,5]TiMe_2^+$, $[CpCMe_2CH_2C_6H_3Me_2\text{-}3,5]TiMe_2^+$, and $[Me_3SiCp CMe_2C_6H_3Me_2\text{-}3,5]TiMe_2^+$ in the solid state [112]. NMR analysis of $[Me_3SiCp CMe_2C_6H_3Me_2\text{-}3,5]TiMe_2^+$ showed exchange of coordinated faces of the aryl group on the NMR time scale, suggesting labile nature of the aryl pendant group.

Huang also conducted ethylene trimerization by using half-titanocene having pendant thienyl group [113]. Although the complex with 1-thienyl group (Chart 5.8 **8c**) catalyzes selective formation of 1-hexene (84 wt% at 30 °C, 156 kg $(\text{mol Ti})^{-1}$ h^{-1}, Table 5.2, run 24), but catalyst with 2-thienyl group forms 1-hexene in 12 wt%, accompanied by the formation of polyethylene. Similar half-titanocene complexes with ether pendant also promote ethylene trimerization, but the activity is lower than those with thienyl group (25–57 kg $(\text{mol Ti})^{-1}$ h^{-1}) [114].

The Ti-catalyzed trimerization of ethylene using the complex with a Cp ligand having aryl pendants also proceeds via a metallacycle mechanism (Scheme 5.8). Neutral trichlorotitanium(IV) complex is converted into the cationic Ti(II) species with an ethylene ligand (Scheme 5.8i) which initiates the catalytic ethylene trimerization [115]. The aryl pendant group assists to make the above reaction smooth by decoordination and recoordination.



Scheme 5.8 Proposed mechanism for the Ti-catalyzed ethylene trimerization

DFT calculation of the ethylene trimerization by a cationic ($C_6H_5CH_2C_5H_4$)Ti fragment supported the mechanism involving metallacycloheptane, formed by oxidative cyclization of Ti complex with ethylene followed by ethylene insertion [116]. Formation of 1-hexene from the titanacycloheptane intermediate occurs via direct β-hydrogen shift rather than via the β-hydrogen elimination/reductive elimination. The β-hydrogen shift takes place through a transition state with a nearly-linear C–H–C arrangement. Formation of 1-butene from a titanacyclopentane intermediate takes place via the other two-step pathway (β-hydrogen elimination/reductive elimination). High energy barrier for this pathway (41 kcal mol^{-1}) renders the formation of 1-butene difficult. The reaction of ethylene with titanacycloheptane to give titanacyclononane is also disfavored compared to the elimination of 1-hexene from titanacycloheptane. Thus, 1-hexene is produced predominantly from the reaction. The pendant arene moiety is more strongly bound to the Ti(II) species rather than the Ti(IV) species of the reaction. The role of the pendant arene is to reduce the olefin coordination energy and thus to promote 3,7-hydrogen shift over further growth of the metallacycle.

DFT (B3LYP functional) studies of the Ti-catalyzed ethylene trimerization concluded the mechanism involving β-hydrogen shift rather than β-hydrogen elimination and reductive elimination [117]. They also suggested easier β-hydrogen shift from the titanacycloheptane and high barrier for the formation of 1-butene from titanacyclopentane complex, due to the geometrical constraints in opening the five-membered metallacycle. The rate-determining step is the ring-opening reaction of the seven-membered metallacycle (barrier is 18.4 kcal/mol). Replacement of the aryl pendant group of the ligand with a non-coordinating methyl group changes the favorable product to polyethylene, which is in agreement with the experimental results.

Tobisch investigated on comparison of the possibilities for the titana(IV)cycle intermediates to cause growth or to decompose affording α-olefins as a function of their ring size, prediction of the favorable route for precatalyst activation, and exploration of the cycloalkane production as a possible side process, by using a gradient-corrected DFT method [118–121]. Metallacycle growth through bimolecular ethylene uptake and subsequent insertion displays very similar structural and energetic characteristics for five- and seven-membered titana(IV)cycles. Decomposition of titana(IV)cycles to α-olefins preferably takes place via a concerted transition-metal-assisted β-hydrogen shift for conformationally flexible metallacycles, with the barriers having to be overcome. The rigid five-membered titana(IV)cyclopentane, however, does not undergo the β-hydrogen shift due to the kinetic barrier and chooses further ethylene insertion, forming the titana(IV)cyclopentane with a seven-membered ring. On the basis of the detailed insights into the ability of titana(IV)cycles to undergo either growth or decomposition to α-olefins, the thermodynamic and kinetic aspects for the selectivity control of the linear ethylene oligomerization have been rationalized.

Quite recently, Kawamura and Fujita reported that Ti complex with phenoxy-imine ligand with pendant aryl-OMe pendant **8a** (Chart 5.8) is effective for trimerization of ethylene to give 1-hexene with very high productivity (6,590 kg (g Ti)$^{-1}$ h^{-1}) (Table 5.2, run 25) [12, 122]. Selectivity for C6 product is 92.3 wt%. Similar complex with aryl-OPh pendant shows lower activity to form a considerable amount of polyethylene. DFT calculations suggest that Ti–OR bond distance is shorter in the complex with aryl–OMe group than aryl–OPh group. Ethylene pressure studies indicate second-order dependence of productivity on ethylene pressure, which support the metallacyclic mechanism. The byproducts other than polyethylene contain dodecene (2-butyl-1-hexene, mainly (ca. 90 wt%)), formed by cotrimerization of 1-hexene with ethylene.

5.3.3 Tantalum Catalyst

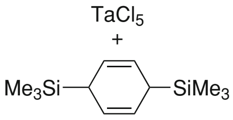
In 2001, Sen reported that $TaCl_5$ in combination with alkylating agents promotes selective trimerization of ethylene in the absence of a ligand [123] (Chart 5.9 **9a**). The reaction proceeds at 45–60 °C under 700 psi of ethylene to produce a mixture of 1-butene, 1-hexene, and 1-octene, where the selectivity for 1-hexene is >94 % (TOF in 385–460 mol (mol Ta)$^{-1}$ h^{-1}, Table 5.2, run 26, 27). Alkylating reagents, Me_4Sn, Me_2Zn, Me_3Al, and alkyl lithiums are effective as the additive. Higher alkylating reagents and alkyl lithium are less useful.

The mechanism of generation of the active species in the catalysis is proposed as shown in Scheme 5.9. It involves reduction of Ta(V) to Ta(III) in the reaction of $TaCl_5$ with the alkylating agents, formation of tantalum(V) metallacyclopentane by the reaction of Ta(III) with two molecules of ethylene. Insertion of another molecule of ethylene to its carbon–tantalum bond, β-hydrogen elimination to

Chart 5.9 Representative Ta catalyst for ethylene trimerization

$TaCl_5$
+
Me_4Sn, Me_2Zn, Me_3Al, RLi

9a



9b

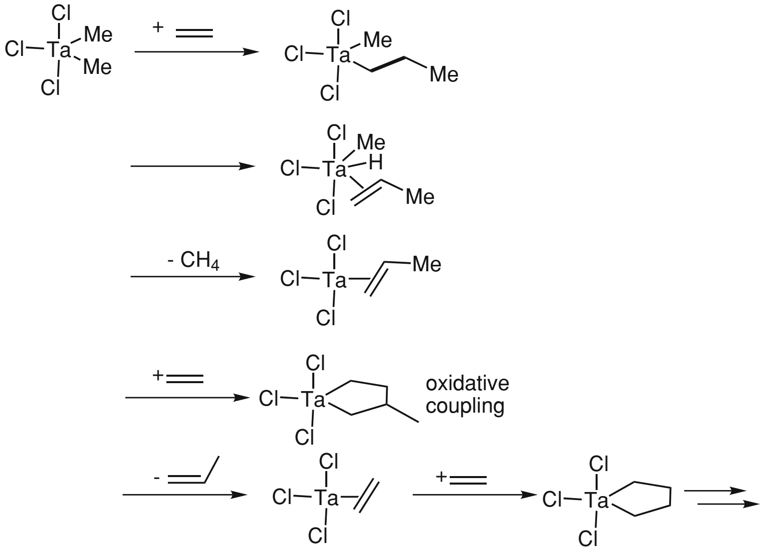
afford Ta(V) alkylhydride, and reductive elimination to afford 1-hexene with regeneration of Ta(III).

MP2 and B3LYP calculations clarified details of the ligand-free reaction [124]. As shown in Scheme 5.9, dimethyltantalum complex, formed by the metathesis of $TaCl_5$ with methylating agents, adopts trigonal bipyramids with two Cl ligands at the axial positions. It allows insertion of ethylene to its methyl-tantalum bond via Cossee mechanism, followed by β-hydrogen elimination to give Ta(III) species with liberation of methane. After formation of the Ta(III) species, the catalytic cycle starts, similarly to those shown in Cr- and Ti-catalyzed selective trimerization of ethylene. Tantalacyclopentane complex is transformed to tantalacycloheptane complex by the insertion of ethylene ($E_a = 13.0$ kcal mol^{-1}). Further ethylene insertion of tantalacycloheptane to tantalacyclononane requires energy barriers of 36.3 kcal mol^{-1}, which is much larger than that of the transformation of tantalacycloheptane to $TaCl_3$(1-hexene) accompanied by elimination of the product (25.5 kcal mol^{-1}). Thus, trimerization is favored rather than tetramerization and dimerization.

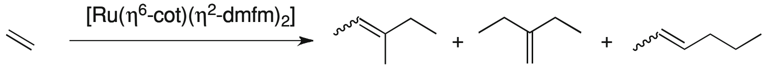
Recently, Mashima reported that catalysts composed of $TaCl_5$ in combination with bis(trimethylsilyl)cyclohexadiene (Chart 5.9 **9b**) or its derivatives promote selective trimerization of ethylene to give 1-hexene [125]. The selectivity for 1-hexene is up to 98.5 % and TOF is up to 1,008 mol (mol Ta)$^{-1}$ h^{-1} (Table 5.2, run 28, 29). Similar to the above catalytic system, Ta(III) species is formed by the reaction of $TaCl_5$ and bis(trimethylsilyl)cyclohexadiene, which is active species of the reaction. In situ NMR analysis of the mixture of $TaCl_5$ and bis(trimethylsilyl)cyclohexadiene in the presence of ethylene at −10 °C shows the formation of tantalacyclopentane. Upon warming the reaction mixture to room temperature, the signals due to the metallacycle disappear and those due to 1-hexene become observable. The formation of Ta(III) species is also supported by the isolation of the corresponding alkyne complex.

5.3.4 Ruthenium Catalyst

Transition metal catalysts other than Cr, Ti, and Ta, which are active for selective trimerization of ethylene, are very limited. Recently, however, Kondo reported Ru(0) complex brings about selective trimerization of ethylene (Scheme 5.10) [126]. The product is a mixture of isohexenes (94 %) and 2-hexene (6 %). The catalyst also promotes codimerization of ethylene with 1-butene or (*E*)-2-butene to give isohexene.



Scheme 5.9 Formation of tantalacyclopentane complex in the reaction of $TaCl_3Me_2$ and ethylene

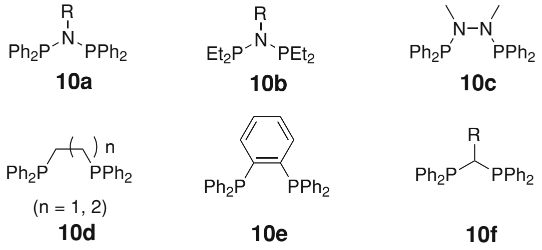


Scheme 5.10 Trimerization of ethylene by ruthenium catalyst

5.4 Tetramerization of Ethylene

Cr complexes with the PNP ligands are one of the most effective catalysts for trimerization of ethylene, giving 1-hexene selectively. As mentioned above, the trimerization proceeds via a metallacycloheptane intermediate, which undergoes β-hydrogen shift or β-hydrogen elimination/reductive elimination. Although insertion of another ethylene molecule to the metallacycloheptane would lead to 1-octene, via metallacyclononane, such selective tetramerization is much rarer than the trimerization. A nine-membered ring is the most unfavored medium-sized ring in organic chemistry, and formation of the metallacyclononane was considered to an unfavorable process. Recently, Cr complexes with special PNP ligands have been found to catalyze tetramerization of ethylene effectively.

Chart 5.10 Representative ligands for Cr-catalyzed ethylene tetramerization



5.4.1 *Effect of Ligand Structure*

The catalyst prepared from $CrCl_3(thf)_3$ bis(diphenylphosphino)amine (PNP), and MAO (Chart 5.10 **10a**) causes ethylene oligomerization to give 1-octene and less amount of 1-hexene [127, 128]. The isolated Cr catalyst adopts dimeric structure $[(\mathbf{10a})CrCl_2]_2(\mu\text{-}Cl)_2$ and shows activity for tetramerization in the presence of MAO [127]. The PNP compounds with 3- and 4-methoxyphenyl groups at the P atom also function as the catalyst ligand for ethylene tetramerization. The ligands with varieties of *N*-substituents have been examined for the catalyst (Table 5.3, runs 1–12) [129–131]. The catalysts with an N–H group afford a mixture of α-olefins with broad distribution, without specific selectivity for C6 and C8, probably due to the deprotonation of NH group. On the other hand, introduction of methyl group on N atom increases C8 selectivity to 59.0 % (94.1 % α-selectivity) and C6 selectivity to 24.8 % (39 % α-selectivity) and 55 % cyclic products (Table 5.3, run 1).

Substituent on the N atom affects the catalyst productivity and selectivity [129]. The ligand with a longer alkyl group on the N atom improves catalytic activity, but the selectivity is not so much influenced (Table 5.3, runs 2, 3). Highest α-selectivity of C8 products is obtained by the ligand with isopropyl and cyclohexyl substituents (α-selectivity >99 %), indicating secondary alkyl substituent on N atom increases the α-selectivity (Table 5.3, runs 4, 5). Alkyl groups with β-branching such as benzyl group also increase the α-selectivity of C6 by decreasing the amount of cyclic product. Although the above reactions are conducted in toluene, the use of methylcyclohexane solvent greatly improves the catalytic activity [129].

Activity and selectivity of the Cr catalyst of bis(diphenylphosphino)amine ligand with an *N*-cycloalkyl substituent are affected by its ring size [130]. The catalysts with smaller size ring (cyclopropyl and cyclobutyl) at the N atom cause lower α-selectivity for both C6 and C8 products with lower productivity (Table 5.3, runs 10, 11), whereas the increased α-selectivity and higher productivity are achieved as increasing the ring size of the substituents (Table 5.3, runs 12–14). With *N*-cyclododecyl substituents, the α-selectivity for C6 and C8 products is increased to 84.6 and 99.4 %, respectively, and productivity reaches 757,720 g $(g\ Cr)^{-1}\ h^{-1}$ (Table 5.3, run 14). The selectivity of 1-octene is highest in the reaction using the ligand with an *N*-cycloheptyl group (C8 = 68.1 wt%)

Table 5.3 Tetramerization of ethylene

Run	Ligand	cocat.	Pressure/ atm	Temperature/ °C	Time/ min	Productivity g (g Cr)$^{-1}$ h^{-1}	C6 wt%	C8 wt%	1–C8 wt%	References
1.	**10a** R = Me	MAO	29.6	65	30	26,500	24.8	59.0	94.1	[127]
2.	**10a** R = pentyl	MAO	29.6	65	30	43,600	24.9	58.1	96.8	[127]
3.	**10a** R = decyl	MAO	29.6	65	30	50,000	25.4	59.0	96.5	[129]
4.	**10a** R = ^{i}Pr	MAO	29.6	65	30	11,700	32.7	60.6	99.2	[127]
5.	**10a** R = cyclohexyl	MAO	29.6	65	30	8,050	32.1	59.4	99.3	[127]
6.	**10a** R = Me	MMAO	44.4	60	30	964,000	16.4	54.0	95.9	[129]
7.	**10a** R = Et	MMAO	44.4	60	30	1,020,000	17.5	63.0	97.3	[129]
8.	**10a** R = ^{i}Pr	MMAO	44.4	60	17	1,950,000	16.8	69.5	99.0	[129]
9.	**10a** R = cyclohexyl	MMAO	44.4	60	16.5	2,150,000	19.4	68.3	99.0	[129]
10.	**10a** R = cyclopropyl	MMAO	44.4	60	35	464,396	19.5	62.5	96.5	[130]
11.	**10a** R = cyclobutyl	MMAO	44.4	60	41	390,650	19.2	61.2	97.0	[130]
12.	**10a** R = cyclohexyl	MMAO	44.4	60	25	726,280	18.7	67.2	99.0	[130]
13.	**10a** R = cycloheptyl	MMAO	44.4	60	25	737,536	24.9	68.1	99.0	[130]
14.	**10a** R = cyclododecyl	MMAO	44.4	60	25	757,720	22.6	66.4	99.4	[130]
15.	**10a** R = Ph	MMAO	49.3	60	12	765,900	16.6	61.8	97.1	[131]
16.	**10a** R = Bn	MMAO	49.3	60	9	1,065,300	18.8	63.5	97.2	[131]
17.	**10a** R = $(CH_2)_2OMe$	MAO	1	25	90	241	61	31	>90	[132]
18.	**10a** R = $(CH_2)_3OMe$	MAO	1	25	90	269	62	34	99	[132]
19.	**10a** R = (*o*-OMe)C_6H_4	MAO	1	25	90	616	66	27	97	[132]
20.	**10a**R = CH_2(*o*-OMe)C_6H_4	MAO	1	25	90	1,083	62	24	93	[132]
21.	**10b** R = $(CH_2)_2SMe$	MAO	29.6	80	180	13,800	25.9	49.3	97.7	[133]
22.	**10b** R = $(CH_2)_2SEt$	MAO	29.6	80	180	17,900	18.0	36.8	98.5	[133]
23.	**10b** R = $(CH_2)_3SMe$	MAO	29.6	80	180	14,700	26.8	55.5	98.5	[133]
24.	**10a** R = $(CH_2)_3SMe$	MAO	29.6	80	60	18,600	9.2	33.3	97.0	[133]

(continued)

Table 5.3 (continued)

Run	Ligand	cocat.	Pressure/ atm	Temperature/ °C	Time/ min	Productivity g (g Cr)$^{-1}$ h^{-1}	C6 wt%	C8 wt%	1–C8 wt%	References
25.	**10c**	MAO	44.4	45	30	26,200	25.2	58.5	98.4	[127]
26.	**10d** (n = 1)	MAO	44.4	45	30	24,800	19.7	39.2	96.6	[127]
27.	**10d** (n = 1)	MMAO	49.3	60	–	144,000	15.7		59.3	[134]
28.	**10d** (n = 2)	MMAO	49.3	60	–	13,000	8.6		30.3	[134]
29.	**10e**	MMAO	49.3	60	–	2,240,000	13.0		56.8	[134]
30.	**10f** R = Me	Et_3Al	54.3	60	–	44,080	23.9	34.6	91.3	[136]
31.	**10f** R = hexyl	Et_3Al	54.3	60	–	82,820	18.8	38.4	95.2	[136]
32.	**10f** R = Bn	Et_3Al	54.3	60	–	70,150	21.9	30.8	91.3	[136]

(Table 5.3, run 13). The introduction of 2-alkyl substituents on *N*-cyclohexyl group increases formation of 1-hexene over 1-octene in very high productivity (>2,000,000 g (g Cr)$^{-1}$ h^{-1}). This result is in agreement with that the increment of steric bulk in P-substituents favors trimerization rather than tetramerization.

Bis(diphenylphosphino)amine ligands with *N*-aryl substituents are also effective (Table 5.3, run 15) [131]. Similar to the results of *N*-alkyl functionalities, introducing bulky isopropyl substituent on *ortho*-position of the aryl group increases C6 and 1–C6 selectivities from 16.6 and 54.2 % to 33.4 and 85.4 %, although the catalyst productivity drops from 765,900 to 159,600 g (g Cr)$^{-1}$ h^{-1}). The use of *N*-benzyl group instead of *N*-phenyl group does not show any remarkable change in product selectivity, but the catalyst productivity is increased to 1,065,300 g (g Cr)$^{-1}$ h^{-1} (Table 5.3, runs 16). Furthermore, the ligand with *N*-phenethyl group improves α-selectivity (84.3 %) compared to that with *N*-benzyl group (70.5 %) without significant loss of productivity (1,001,600 g (g Cr)$^{-1}$ h^{-1}). On the whole, PNP ligands with *N*-aryl functionality show lower selectivity than their *N*-cyclohexyl analogues, both in terms of overall α-octene formation and overall α selectivity.

The complexes with methoxyalkyl or methoxyaryl group on N atom show lower activity than favor formation of C6 product (61–66 wt%) rather than C8 product (24–34 %), but the increased ethylene pressure favors 1-octene production (Table 5.3, runs 17–20) [132]. Similar complexes with thioether pendant on N atom (Chart 5.10 **10d**), in contrast, promote ethylene tetramerization (C8 = up to 55.5 wt%) in the presence of MAO (Table 5.3, runs 21–24) [133]. In contrast, thiophenyl group results in increased selectivity (68.3 %). Organoaluminum cocatalysts other than MAO, such as MMAO and EAO, are usable as the cocatalyst. In addition to PNP ligand, PNNP ligand (Chart 5.10 **10c**) is effective for tetramerization (Table 5.3, run 25).

Overett reported varieties of carbon-bridged diphosphine ligands for the ethylene oligomerization including tetramerization [134]. Although Cr-dppm complexes give ethylene oligomers with Schulz–Flory distribution (α = 0.55), the catalysts with dppe and dppp form 1-octene in 59.3 and 30.3 wt%, respectively, with lower activity (144,000 and 13,000 g (g Cr)$^{-1}$ h^{-1}) and increased formation of polyethylene compared to PNP (Table 5.3, runs 26–28). Use of 1,2-diphenylphosphinobenzene **10e** causes the tetramerization in high productivity (Table 5.3, run 29) [134].

Cr catalysts with PNP ligand are used for both ethylene trimerization and tetramerization (Chart 5.4 and 5.10). The key for the formation of 1-octene rather than 1-hexene is the P-substituents of the ligand. The ligand with *ortho*-methoxyphenyl substituents on P atom causes selective trimerization, and that with *para*-methoxyphenyl substituents enhances tetramerization rather than trimerization. It may be due to the steric crowding around the catalytic center or by pendant coordination of a donor substituent.

P–Cr–P bite angle is related to the oligomerization results. The bis(diarylphosphino)amine ligand, which forces small bite angles (ca. 67°), shows the highest 1-octene:1-hexene ratios (ca. 9.1:1), although the ratio is largely influenced by the *N*-substituent. The 2-carbon spacer ligands, such as dppe are typically coordinated by transition metals with the P–M–P bite angles of 81–83°, and produce slightly more 1-hexene at the expense of 1-octene. The 3-carbon spacer ligands with still larger bite angles—typically ca. 91° for dppp, gave the lowest 1-octene:1-hexene ratios. Bis(diphenylphosphino)benzene show very high catalyst activity in those carbon spacer ligands, but the selectivity is inferior compared to the bis(diarylphosphino)amine ligand due to increased formation of C6 cyclic products and low 1-octene to 1-hexene ratio. Similar 1,2-phenylene bridged ligand with P-(2-ethylphenyl) group or P-isopropyl group leads to the increased selectivity for trimerization of ethylene (1-hexene = 59.2 and 82.8 %, respectively). The use of bis(diisopropylphosphino)ethane and bis(dimethylphosphino)ethane ligand also shifts the reaction from tetramerization to trimerization, compared to dppe. Oligomerization using dppm lacks selectivity, but bis(diisopropylphosphino)methane, with more basic nature, is effective as ligand for selective tetramerization. Thus, both steric and electronic factors are important in the selectivity.

Cheong employed Cr complexes with stereoisomers of 1,2-dimethyl-1,2-bis(diarylphosphino)ethane ligands and obtained catalytic activity of 274–2,256 kg (g Cr)$^{-1}$ h^{-1} for ethylene tetramerization [135]. The *racemo*-(*S,S*) or (*R,R*) complexes show higher activity and 1-octene selectivity than *meso*-(*S,R*) complex. The complex with *racemo*-1,2-dimethyl-1,2-bis(diphenylphosphino)ethane ligand shows catalytic activity of 1,929 kg (g Cr)$^{-1}$ h^{-1}), which is higher than that using PNP (282 kg (g Cr)$^{-1}$ h^{-1}) under the same conditions, and good selectivity for 1–C8 (59.2 %). X-ray crystallography and DFT calculation showed smaller PCCP dihedral angle and smaller P–Cr–P bite angle of racemo complex compared to the meso complex.

In line with the founding by Overett, the product obtained by Cr dppm complex is a Schulz–Flory distribution mixture. Wass reported the synthesis of cationic Cr(I) complexes with alkylated dppm ligands and their use for ethylene oligomerization [136]. The complexes with alkyl group attached to carbon bridge of the ligand afford C8 product mainly (30.8–38.4 %), although their selectivity and activity (44,080–70,150 g (g Cr)$^{-1}$ h^{-1}) are inferior to that with PNP ligand (Table 5.3, runs 30–32).

Hanton obtained $[Cr(CO)_4(PNP)][Al\{OC(CF_3)_3\}_4]$ by the reaction of $Cr(CO)_4(PNP)$ with $Ag[Al\{OC(CF_3)_3\}_4]$, and analyzed its structure by X-ray crystallography [137]. The complex promotes tetramerization of ethylene in the presence of $AlEt_3$, although similar complexes with PF_6 or BF_4 counter anion are not active.

5.4.2 *Effect of Cocatalysts and Additives*

Various cocatalysts were examined for the ethylene trimerization/tetramerization catalyzed by the Cr complexes. $AlEt_3$-based cocatalysts for the reaction using a mixture of $CrCl_3(thf)_3$, bis(diphenylphosphino)isopropylamine as the catalyst change the selectivity from 90 % C6 to 72 % C8 depending on the cocatalysts [138, 139]. $B(C_6F_5)_3$ and $Al(OC_6F_5)_3$ are not suitable for the cocatalysts, but $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ affords highly active and long-lived catalysis system.

Jiang reported addition of tetrachloroethane (10 mol equiv. with respect to Cr) to the PNP/Cr/MAO system improved selectivity of 1-octene from 71.8 % (activity = 18.8×10^6 g (mol cat.)$^{-1}$ h^{-1}) to 74.9 % (activity = 3.42–18.8×10^6 g (mol cat)$^{-1}$ h^{-1}) [140]. Dichloromethane and 1,1,2-trichloroethane are superior with respect to 1-octene selectivity and catalytic activity, compared to trichloromethane, tetrachloromethane, and 1,1,1-trichloroethane [141]. These chlorides work better than the corresponding bromides. These alkyl chloride additives were proposed to coordinate to two chromium centers of the dinuclear complex to change this structure a more suitable one for ethylene tetramerization.

5.4.3 Mechanism of Cr-Catalyzed Ethylene Tetramerization

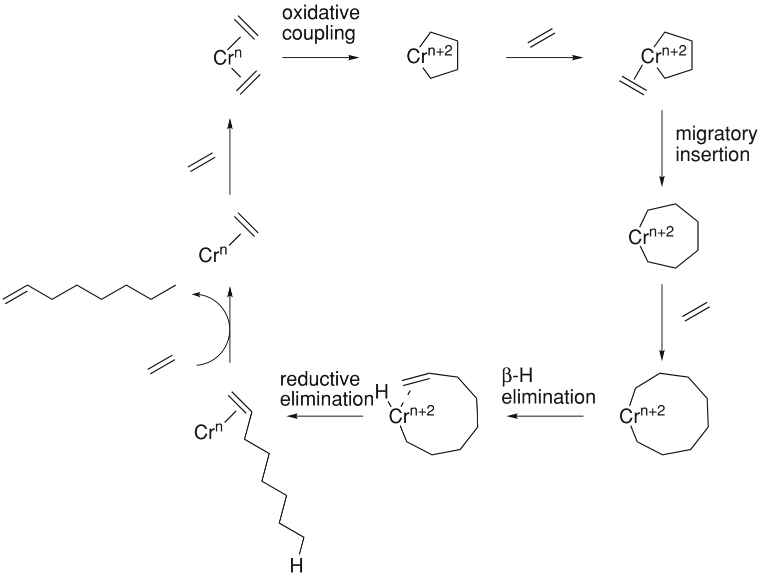
Scheme 5.11 shows the proposed mechanism for ethylene tetramerization. Detailed studies on the reaction products rationalized formation of 1-butene, 1-hexene, methylcyclopentane, methylenecyclopentane, 2-propenylcyclopentane, n-propylcyclopentane, and C10, C12, and C14 secondary oligomerization products [142]. The reaction of a mixture of C_2H_4 and C_2D_4 and analysis of the methylcyclopentane isotopomer distribution revealed that the reaction proceeds via metallacycle formation, not via Cossee–Arlman linear chain growth.

Enhanced stability of metallacycoheptane intermediate of the tetramerization relative to that of the trimerization catalysis renders insertion of ethylene, forming 1-octene, competing with formation of C6 products such as 1-hexene, methylenecyclopentane, etc.

Gambarotta isolated a new cationic complex $\{[PNP]_2Cr(\mu\text{-}Cl)AlMe_3\}[ClAlMe_3]_{0.34}[Me_4Al]_{0.66}$ from the reaction mixture of $PNPCrCl_3$ with $AlMe_3$ [143]. Upon addition of MAO, it promotes trimerization and tetramerization of ethylene (C8: 73.4 %) with activity of 8,400 g (g Cr)$^{-1}$ h^{-1}, which is comparable to $[PNP]CrCl_3$/MAO catalyst (8,000 g (g Cr)$^{-1}$ h^{-1}). Similar activity of the Cr(III) precatalyst and the Cr(II) complex for the tetramerization suggests that Cr(III) is reduced to Cr(II) at a preliminary stage of the catalysis.

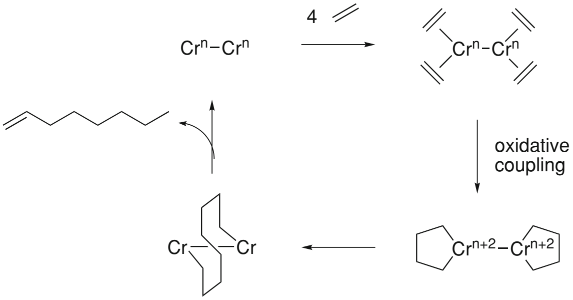
The ligand-to-Cr ratio changed the reactions from selective 1-hexene and 1-octene formation to formation of the oligomers with statistical molecular length distribution. The product under the ligand/Cr ratio of 0.5 obeys molecular weight with Schulz–Flory distribution [144]. Moreover, odd numbered 1-olefin is observed at sub-stoichiometric ratios. These results are accounted for by the formation of binuclear complex $(PNP)Cr_2$ or higher aggregates and/or chromium carbine complex. Scheme 5.12 shows a proposed mechanism for selective ethylene tetramerization.

It involves conversion of dinuclear metallacyclopentane intermediates to a large dinuclear metallacycle species, which causes selective formation of 1-octene [145].



Scheme 5.11 Proposed mechanism for the Cr-catalyzed ethylene tetramerization

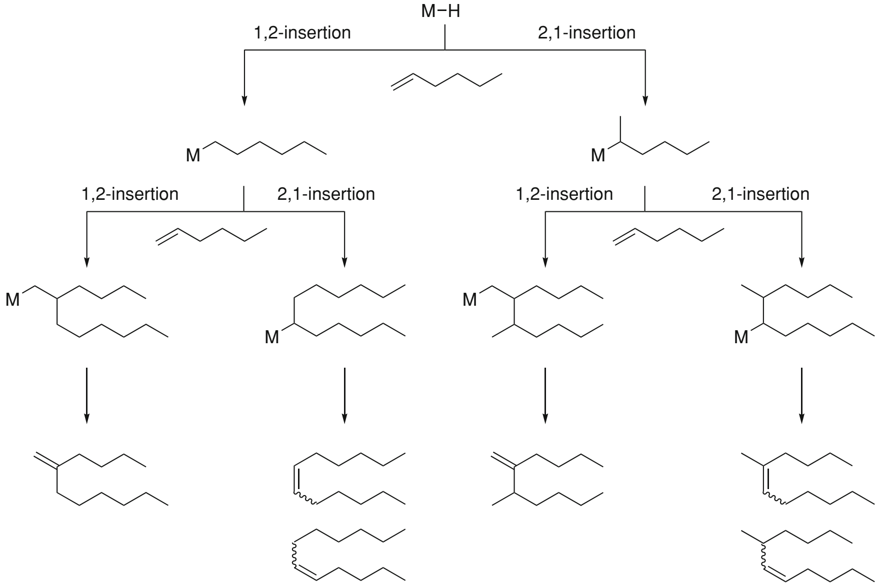
Scheme 5.12 Proposed mechanism involving binuclear Cr complex for the Cr-catalyzed ethylene tetramerization



Two chromacyclopentanes in the catalyst molecule undergo 1,2-reductive elimination to give the dinuclear intermediate, having 1,8-octanediyl ligand. Elimination of 1-octene regenerates the dichromium catalyst precursor.

5.5 Dimerization of α-Olefins

Oligomerization of α-olefins produces linear and/or branched products depending on the regiochemistry of the monomer insertion to the metal-carbon bond. Scheme 5.13 summarizes relationship between regiochemistry and structure of the product formed by 1-hexene dimerization via Cossee mechanism. First 1,2-insertion of 1-hexene to metal-hydride bond, followed by 2,1-insertion of the



Scheme 5.13 Relationship between regiochemistry and structure of the product in 1-hexene dimerization

monomer and β-hydrogen elimination leads to the linear product, whereas the successive 1,2-insertion of the two monomer molecules yields the branched product with a vinylidene group. Generally the products contain vinylene (inner olefin) and/or vinylidene (*exo*-methylene) groups. Studies on the dimerization of α-olefins were reported by several groups.

Reaction of ethylene and α-olefins by using zirconocene/MAO catalysts generally produces the copolymers. On the other hand, Bergman reported formation of the selective dimeric products (80–90 % yield) in the reaction under low Al/Zr ratio (ca. 1:1) [146]. The produced codimer contains *exo*-methylene group, and formed via double 1,2-insertion of the α-olefin into the Zr–H and Zr–C bond. The presence of Cl ligand rather than alkyl ligand at the zirconium center is proposed, which makes β-elimination easier than further insertion of olefin.

Ni complex with 1,3-diketonate ligand (Chart 5.11i), which has been known as the common catalyst for ethylene oligomerization, promotes dimerization of α-olefins in the absence of cocatalyst to give linear dimer predominantly (62–85 %) [147]. Higher olefins show decreased reactivity (128–770 mol (mol Ni)$^{-1}$ h^{-1}). Preferential formation of the linear dimer indicates the reaction proceeds via 1,2-insertion of the first olefin to Ni–H bond followed by 2,1-insertion of the second to the Ni–C bond. Although the catalyst loses its activity at room temperature, it can be stored as toluene solution at 0 °C without significant decomposition for over 30 days [148]. Activity of the Ni catalyst is improved by using it (up to TOF = 2,100 mol (mol Ni)$^{-1}$ h^{-1}) in the buffered ionic liquid [149]. High

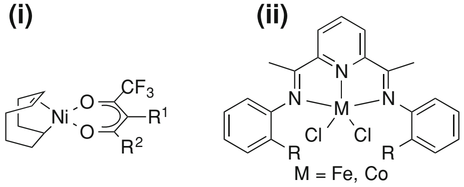


Chart 5.11 The catalysts for linear dimerization of α-olefins

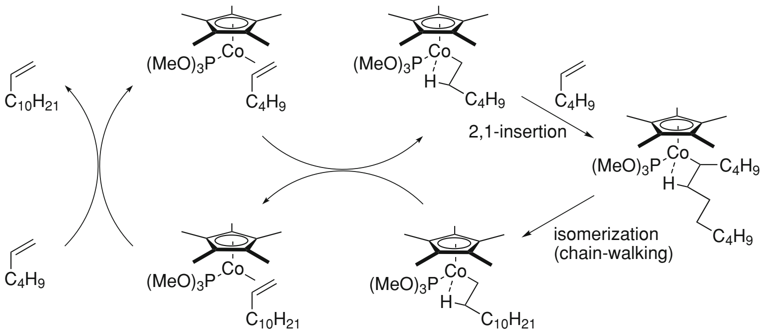
selectivity for dimerization (98 %) and linearity (64 %) is maintained. Biphasic reaction medium also allows easy catalyst recovery and recycling. Diimine Ni complexes, which are active for ethylene oligomerization, promote dimerization of propylene. The products are a mixture of linear and branched olefins, as a result of 1,2- and 2,1-insertion of the monomer into Ni–H and/or Ni–C bond.

Small reported the iron and cobalt complexes with bis(imino)pyridine ligands are effective for linear dimerization [150] (Chart 5.11ii). The complexes with bulky substituents at the ligands show high activity for ethylene polymerization. The iron complex also promotes polymerization of propylene, which proceeds via 2,1-insertion of the monomer to the Fe–C bond. In contrast, bis(imino)pyridine iron complexes with less sterically hindered aryl groups are effective for oligomerization of ethylene (Sect. 5.2.2 of this chapter and Chart 5.2ii) and head-to-head dimerization of various α-olefins such as propylene, 1-hexene, and 1-decene to afford the corresponding linear dimers as main product (up to 80 %). The mechanism of the reaction involves selective 1,2-insertion of α-olefin into the iron-hydride bond and 2,1-insertion of the olefin into the metal-carbon bond, followed by chain transfer via β-hydride elimination. The methyl-branched dimers also form as a result of successive 2,1-insertion of the α-olefin.

The bis(imino)pyridine cobalt complexes are also active for the dimerization of α-olefins [151]. Although the activity is lower than the corresponding iron complexes, linearity of the product is higher (>97 %). In the reaction of 1-butene, 1-hexene, and 1-decene, the dimeric products are formed in high selectivity (>82 %). The reaction mechanism is similar to Fe-catalyzed linear dimerization of α-olefins. In contrast, the reaction of propylene produces not only linear dimer, but also trimers, teramers, and pentamers. Interestingly, all of the oligomers are of high linearity (>93.5 %). Formation of such linear higher olefins is accounted for by the successive 2,1-insertion of propylene and 1,2-shift of the Co center (chain growth pathway) and/or the linear codimerization of once-formed 1-hexene (step growth pathway).

Gibson also reported the bis(imino)pyridine Co catalyst for the dimerization of 1-butene and 1-hexene to give the corresponding linear dimer with internal olefinic group (rich in E isomers) [152]. The reaction of propylene leads to 1-hexene without isomerized product, similarly to the results by Small. The formation of linear trimers and tetramers also form during the reaction, as a result of combined chain growth and step growth mechanism. The complexes with fluorinated aryl imino group show much higher catalytic activity than the nonfluorinated counterpart.

Although inner olefins are frequently formed in the dimerization of α-olefins, Broene recently reported that half cobaltocene complex with $P(OMe)_3$ ligand



Scheme 5.14 Proposed mechanism for the formation of 1-decene in Co-catalyzed dimerization of 1-hexene

promotes dimerization of 1-hexene to give 1-decene as a byproduct [153] (Scheme 5.14). The main product is 2-butyl-1-octene, which is formed by double 1,2-insertion of 1-hexene to Co–H and Co–C bonds. In contrast, 1-decene is formed via 1,2-insertion of 1-hexene to Co–H and 2,1-insertion of the monomer to Co–C bond, followed by isomerization of secondary alkyl Co species to primary alkyl Co species. The isomerization is considered to proceed via β-hydrogen elimination and re-insertion, similar to the olefin polymerization catalyzed by Pd and Ni complexes with diimine ligands (chain walking).

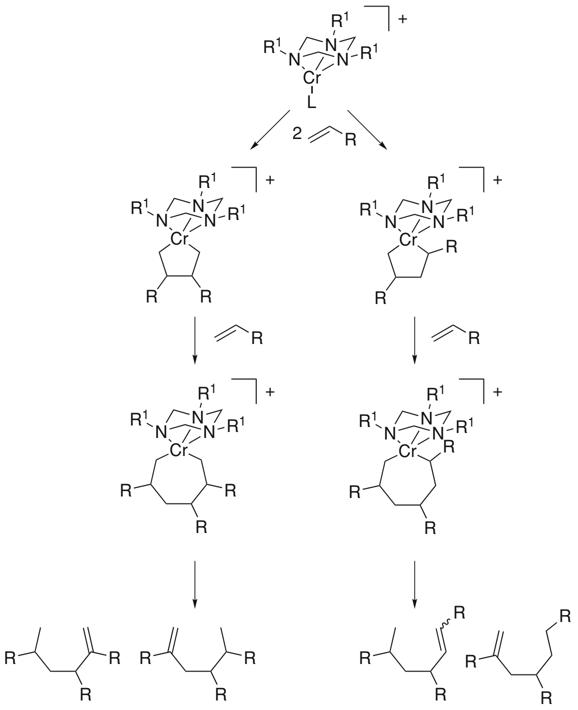
The Ta-catalyzed dimerization of olefins was also reported by Schrock in 1980 [154]. The reaction proceeds via metallacycle mechanism, similar to the Ta-catalyzed trimerization of ethylene. The product is a mixture of tail-to-tail dimer and head-to-tail dimer. In the case of propylene, 1-pentene, and 1-octene the major product is the tail-to-tail dimer (86–98 %), whereas the reaction of 4,4-dimethyl-1-pentene results in selective formation of head-to-tail dimer (100 %). The activity of the catalyst is on the order of one turnover/h at 30 °C.

5.6 Trimerization of α-Olefins

Although many reports on ethylene trimerization have appeared in the literatures, examples of trimerization of α-olefins are very limited. In 2000, Köhn reported that Cr complexes with triazacyclohexane ligand in combination with MAO promote trimerization of α-olefins [155, 156]. The product is a mixture of the isomers of α-olefin trimers. At room temperature, the trimerization stops after a few hours (about 1,000 turnovers) caused by decomposition of the catalyst, while the catalyst keeps its activity for several days at 0 °C (conversion reaches >90 %).

The plausible reaction mechanism involves formation of cationic Cr(I) species and formation of metallacycle intermediate by oxidative cyclization, similar to the

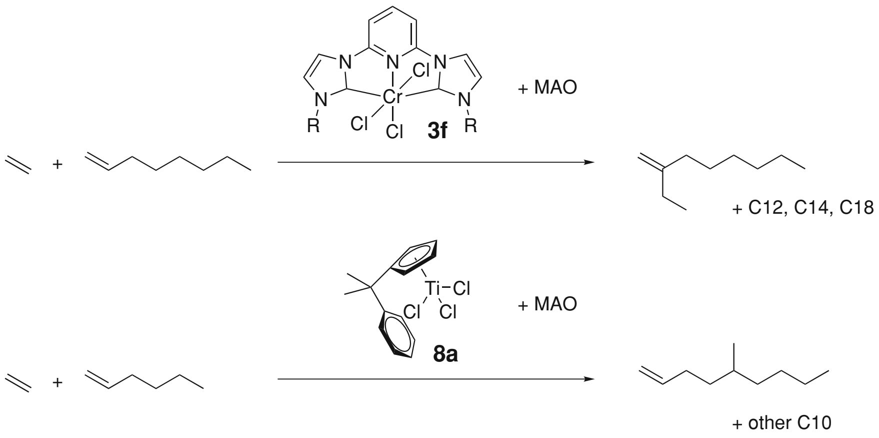
Scheme 5.15 Codimerization of ethylene with α-olefins



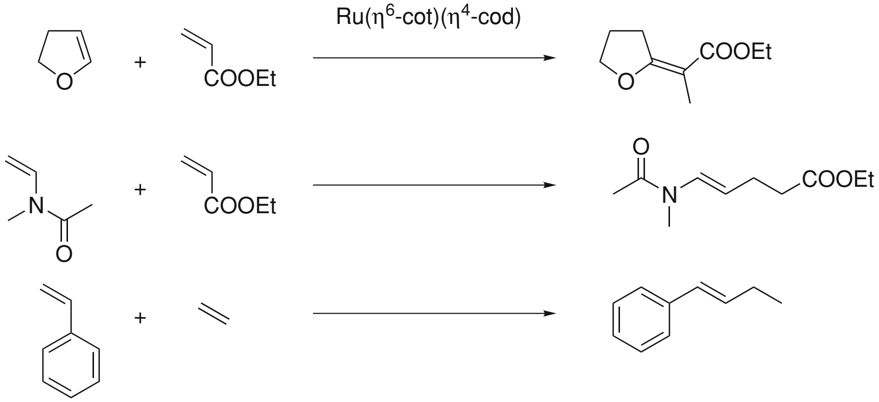
ethylene trimerization (Scheme 5.15). The rate-determining step is insertion of the third olefin to Cr–C bond, which is followed by β-hydrogen elimination and reductive elimination of the α-olefin trimers. The activity and selectivity of the catalysts are largely affected by the alkyl group of the ligand. Branched structure in the α-position of the alkyl group increases isomerization rather than trimerization, and decreases activity of the catalyst.

5.7 Cooligomerization of Ethylene and α-Olefins

In principle, reaction of ethylene and α-olefins can afford the corresponding cooligomer, but the actual examples are very limited. Cr complex with bis(carbine)pyridine ligand promotes codimerization of ethylene with 1-octene via metallacycle mechanism [128] (Scheme 5.15). The product contains not only 2-ethyloct-1-ene, formed by the reaction of ethylene with 1-octene, but also C12, C14, and C18 products (cotrimerization and cotetramerization product). Hessen also reported that half titanocene complex promote cotrimerization of ethylene with 1-hexene to give C10 products (5-methylnon-1-ene, mainly) [111] (Scheme 5.16).



Scheme 5.16 Ru-catalyzed codimerization of vinyl monomers



Scheme 5.17 .

5.8 Cooligomerization of Other Vinyl Monomers

Codimerization of ethylene with various vinyl monomers (hydrovinylation) has been known [157, 158]. The catalyst for the hydrovinylation involves Ni, Pd, and Ru. Examples of asymmetric hydrovinylation have been also reported [159]. Recently, Kondo revealed that ruthenium catalysts catalyze codimerization of different vinyl monomers in very high selectivity [160]. For example, $RuCl_3$(tpy)/Zn (tpy = 2,2′:6′2″-terpyridine) promote codimerization of norbornene with acrylates [161]. Ru(cod)(cot) is effective for codimerization of dihydrofuran and *N*-vinylacrylamide with acrylates (Scheme 5.17) [162]. Codimerization of ethylene with styrene catalyzed by Ru(cod)(cot) yields 1-phenyl-1-butene [163], which is in contrast to that 3-phenyl-1-butene is obtained in the general hydrovinylation.

5.9 Summary

In contrast to transition metal-catalyzed olefin polymerization, the development of oligomerization catalysts is much less matured. In this decade, novel highly active and selective ethylene oligomerization catalysts have been disclosed, which enabled selective formation of 1-hexene and 1-octene from ethylene in high catalytic activity. There are still rooms for investigation in selective synthesis of higher α-olefins by ethylene oligomerization and selective oligomerization of α-olefins. Further development of novel oligomerization catalysts is expected.

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Chapter 6
Polymerization of Polar Monomers

Kyoko Nozaki

Abstract This chapter reviews recent progress in the coordination polymerization of vinyl monomers bearing polar functional groups and their copolymerization with ethylene. Sm and Zr complexes with cyclopentadienyl ligands catalyze the production of poly(methyl methacrylate) (PMMA) from methyl methacrylate (MMA) as well as a block copolymer of ethylene with MMA. The structure of PMMA is controlled to be syndiotactic by chain-end control. Pd complexes with diimine ligands catalyze the copolymerization of ethylene with methyl acrylate (MA); the resulting polymer contains the MA unit as a terminal group of some of the polymer branches. Neutral Pd complexes with chelating monoanionic phosphine-sulfonate ligand enable the copolymerization of ethylene with various vinyl monomers with polar functional groups. The copolymerization of ethylene with methyl acrylate (MA) catalyzed by a Pd/phosphine-sulfonate complex produces a random copolymer that contains MA monomer units at various densities (up to 52 %) in the main chain. Experimental and theoretical approaches to elucidating the polymerization mechanism revealed details of the polymer growth. The catalyst can be used for the copolymerization of ethylene with other polar monomers such as vinyl acetate, allyl acetate, and acrylonitrile, as well as for the alternating copolymerization of vinyl monomers with CO. A bisphosphine monoxide (BPMO) ligand was found to work as a substitute for phosphine-sulfonate.

6.1 Introduction

The word “polar monomer” is commonly used for a small organic molecule having a vinyl group (CH_2=CH–) and a functional group; representative examples are, methyl acrylate (MA), methyl methacrylate (MMA, although this does not

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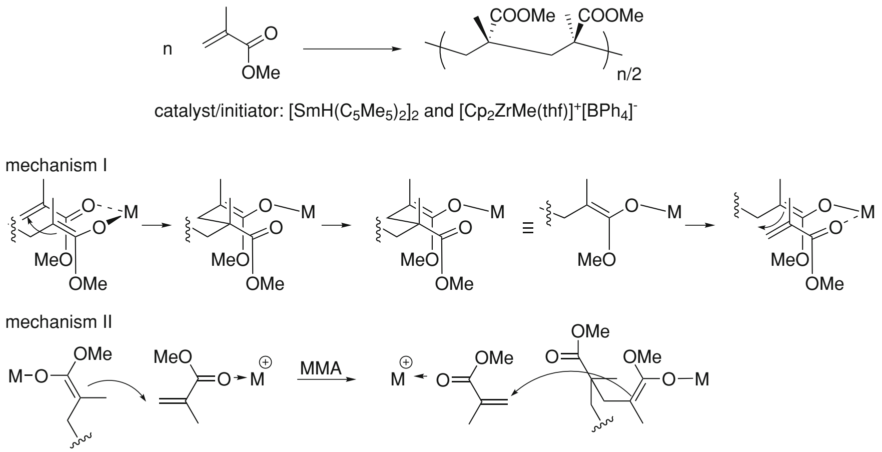
have a vinyl group), acrylamide (AA), acrylonitrile (AN), vinyl acetate (VAc), vinyl halides, and vinyl ethers. While numerous polyolefins such as polyethylene and polypropylene have been synthesized by single-site metal-catalyzed coordination polymerization, development of organometallic reactions applicable to polymerization of polar monomers still remain as a significant challenge in polymer synthesis [1, 2]. Most widely used processes for the polar monomer polymerization utilizes either anionic (for MA, MMA, AA, and AN), cationic (for vinyl ethers), or radical polymerization (for most of the monomers). There have been reported a variety of catalysts and/or initiators developed for anionic [3] and radical [4] polymerization of polar monomers for creating controlled structures.

Considering that the main theme of this book is organometallic reactions, descriptions in this chapter will be focused on coordination polymerization catalyzed by organometallic species, where a monomer coordinates to a metal center in prior to chain propagation [5–11]. First, homopolymerization of polar monomers will be reviewed highlighting group 4 and lanthanide metal catalysts. Among these, a family of catalysts are able to catalyze not only polar-monomer polymerization but also ethylene polymerization thus providing polar-nonpolar block copolymers. On the other hand, random incorporation of polar monomers into polyolefins is of much interest in a view point of modifying chemical property of polyolefins. Recent development of Pd catalysts for this purpose will be next described. Copolymerization of polar monomers with non-vinyl monomers will be described briefly, followed by conclusions and outlook.

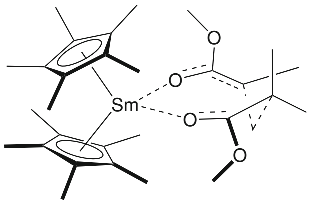
6.2 Coordination-Addition Polymerization of Polar Monomers

Ziegler-Natta type catalyst consists of $TiCl_4$ and AlR_3, well known as most widely used catalyst for polyolefin production, was reported to mediate syndiospecific MMA polymerization at low temperature (-28 to -78 °C) although the active site and the reaction mechanism were not clarified [12]. The first controlled/living methacrylate polymerization was reported by using single-site catalyst $[SmH(C_5Me_5)_2]_2$ [13] and $[Cp_2ZrMe(thf)]^+[BPh_4]^-$ [14]. Syndiotactic PMMA was obtained at 0 °C in $rr = 82.3\ \%$, $M_n = 563{,}000$ ($M_w/M_n = 1.04$) with $[SmH(C_5Me_5)_2]_2$ and $r = 80\ \%$, $M_n = 158{,}000$ ($M_w/M_n = 1.33$) with $[Cp_2ZrMe(thf)]^+[BPh_4]^-$. As a reaction mechanism, two types of repetitive 1, 4-addition of ester enolate was suggested as shown in Scheme 6.1. The first one is a monometallic system described as mechanism I. This mechanism was nicely supported by isolation of MMA-coordinated Sm species, namely $(C_5Me_5)_2Sm(O–C(–OMe){=}CMe_2)(MMA)$ as shown in Fig. 6.1. The second one is a bimetallic system described as mechanism II. For Cp_2Zr catalysts, DFT calculation supported this bimetallic system [15, 16].



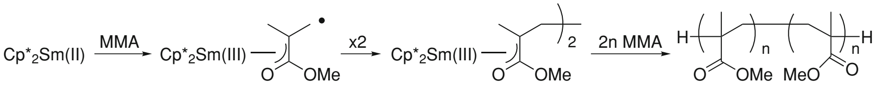
Scheme 6.1 Syndiospecific MMA polymerization

Fig. 6.1 A schematic drawing of isolated $(C_5Me_5)_2Sm[O\text{–}C(OMe)=CMe_2]$ (MMA). The structure was confirmed by X-ray analysis (Ref. 13)



Methyl lanthanocenes, $Cp^*_2LnMe(THF)$ (Ln: Sm, Y, Yb, Lu), and $AlMe_3$ complexes of lanthanocenes, $Cp^*_2Ln(\mu\text{-}Me)_2AlMe_2$ (Ln: Y, Yb, Lu), behave in a fashion similar to that of $[Cp^*_2SmH]_2$ toward MMA polymerization, with the polymerization activity increasing with an increase in ionic radii of the Ln metal (Sm > Y > Yb > Lu) within the series [17]. The MMA polymerization by lanthanocenes is typically carried out in toluene, but polar solvents including THF and Et_2O can also be used in the case of $Cp^*_2SmMe(THF)$ and $Cp^*_2YbMe(Et_2O)$ without noticeably altering the polymerization results, including PMMA syndiotacticity, M_n, and M_w/M_n. This observation is noteworthy because this is *in sharp contrast to* classic anionic polymerization of MMA initiated by organometallic lithium reagents, where solvents play a critical role in determining the tacticity of PMMA produced, especially at low temperatures, due to competition between counterion coordination to chain-end and monomer versus solvation (Scheme 6.2).

When MMA polymerization is initiated by divalent lanthanocenes, such as Cp^*_2Sm and $Cp^*_2Sm(THF)_2$, bimetallic trivalent samarocenes derived from a redox-then-radical-coupling process served as the initiator [17, 18]. Specifically, chain initiation involves one-electron transfer from the Sm(II) center to MMA,

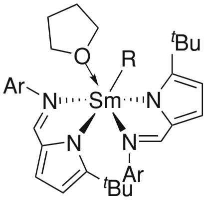


Scheme 6.2 Two-way chain propagation of PMMA initiated by Sm(II)

forming a MMA radical anion and a Sm(III) cation which combine to Sm(III)-enolate complex radicals; the radicals subsequently couple in a tail-to-tail fashion to generate bimetallic Sm(III)-enolate complex, which acts as a bifunctional diinitiator for living polymerization of (meth) acrylates.

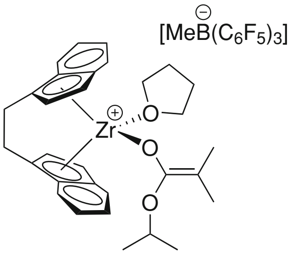
Using preformed bimetallic Sm(III) initiators $Cp*_2Sm$-R-$SmCp*_2$, PMMA and poly(ε-caprolactone) with discrete functionalities at the center of the backbone.

While most of the metallocene catalysts exhibits syndiospecificity in MMA polymerization, high isospecificity (97.8 % mm at 0 °C) was accomplished by bis (pyrrolylaldiminato)samarium **1** [19]. Thus far, the highest performance in a sense of TOF (3,600 h^{-1} at 25 °C), controlled molecular weight $M_n = 75.5$ kD ($M_w/M_n = 1.03$), and mm of 95.3 % was reported with C_2–ansa-metallocene **2** [20]. The polymerization is applicable to methyl acrylate (MA), acryl amide, methacrylamide, acrylonitrile, and vinyl ketone. For further details a review article may be referred [9].



R = CH_2SiMe_3
Ar = 2,6-$^iPr_2C_6H_3$

1



2

In addition to above, many homopolymerization reactions of polar vinyl monomers have thus far been reported, but most of them lack sufficient data to prove that the polymerization proceeded via the coordination polymerization. In fact, no concrete methods are available for differentiating coordination polymerization from other polymerization mechanisms. For example, Yamamoto et al. reported the first "coordination polymerization of polar vinyl monomers" in 1967 followed by a series of reports on Ni, Fe, Co, Ni, Rh, and Cu catalyses [21]. A quarter of a century later, however, some researchers reinvestigated the polymerization of AN and proposed mechanisms that differed from each other, as well as from that proposed by Yamamoto [22]. This remains an unresolved issue, and therefore, it serves as a good example of difficulties involved in elucidating the mechanism of the homopolymerization of polar vinyl monomers.

6.3 Block Copolymerization of Polar Monomers and Non-polar Monomers

Since both ethylene (E) and (meth) acrylate undergoes living homopolymerizations catalyzed by lanthanocenes such as $Cp^*_2SmMe(THF)$ and $[Cp^*_2SmH]_2$, controlled block copolymerizations of E and (meth) acrylates were realized using such lanthanocenes via a two-step polymerization procedure. As shown in Scheme 6.3, the polymerization starts with E under mild conditions (20 °C, 1 atm pressure, toluene) followed by addition of MMA [23]. The E to MMA molar ratio in the resulting block copolymer can be varied in a range of 100:1–100:103 when M_n of the initial PE was fixed to ca. 10,300. When the initial M_n of the PE block is higher, the relative ratio of the PMMA block decreases significantly due to precipitation of PE. This two-step block copolymerization procedure is applicable to the block copolymerization of E with acrylates.

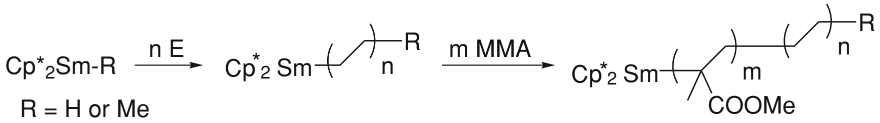
Notable is that this block copolymerization is only one-directional, namely, coordination insertion polymerization of E should be followed by coordination-addition polymerization of polar monomers but not in the reversed order because Sm–O (enolate) adds to polar monomer but not to E. By utilizing the two-way chain-propagation described in Scheme 6.2, ABA-type E/MMA triblock copolymers were obtained starting from divalent ansa-samarocenes (Scheme 6.4) [24].

A diblock copolymer of propylene (P) and MMA was synthesized by two-step mechanisms. While conventional approach employs tandem reaction of metal-catalyzed P polymerization followed by radical MMA polymerization, group 4 metal catalysts enabled coordination-insertion polymerization of propylene followed by coordination-addition polymerization of MMA [25]. Specifically, *rac*-(EBI)-ZrMe+MeB$(C_6F5)_3$ yields *it*-PP-*b*-*it*-PMMA stereodiblock copolymer, whereas (CGC)TiMe+MeB$(C_6F5)_3$ affords *at*-PP-*b*-*st*-PMMA stereodiblock copolymer (Scheme 6.5).

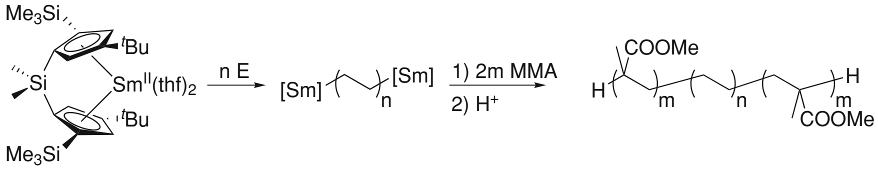
6.4 Random Copolymerization of Polar Monomers and Non-polar Monomers

The polyolefins without any functionality often suffer from the problems associated with insufficient surface properties such as adhesion, dyeability, printability and compatibility. The incorporation of polar functional groups into polyolefins improves such properties, leading to expand the range of applications. For example, polypropylenes modified with less than 1 % of maleic anhydride can make the polymers exhibit better surface properties enough for the application to compatibilizing agents [26]. Thus, the incorporation of polar functional groups into polyolefins is a powerful method to synthesize functional polymeric materials.

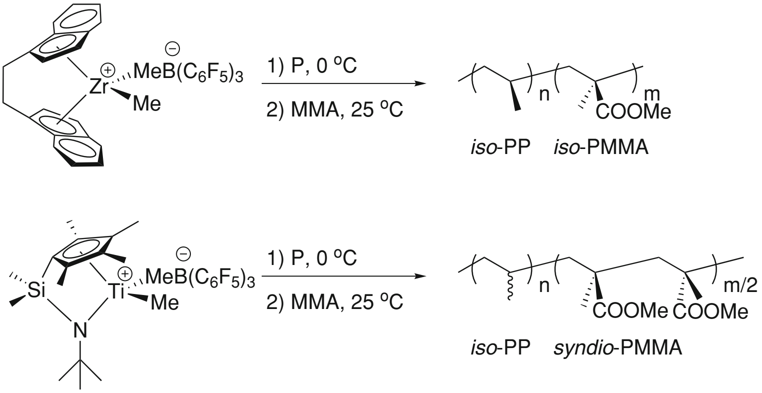
Copolymerization of polar monomers with non-polar olefins is an attractive direct route to the functionalized polyolefins. On the other hand, however, polar



Scheme 6.3 Block Copolymerization of E/MMA Catalyzed by Initiated by Cp*$_2$SmR



Scheme 6.4 Synthesis of ABA triblock copolymer of E/MMA



Scheme 6.5 Synthesis of Stereodiblock PP-PMMA

functional groups often poison active catalysts of olefin polymerization by their strong coordination to the metal centers. Therefore, there is a strong requirement for novel catalysts capable of copolymerizing polar monomers with non-polar monomers via controlled coordination polymerization processes that would yield polymers with novel architectures and properties.

The use of late transition metal catalysts is an alternative possibility. Owing to their reduced oxophilicity and tolerance to other functionalities, these catalysts enable us to utilize functional monomers without protection. Thus far, several promising late transition metal catalysts, especially palladium complexes, have been developed and utilized for the copolymerization of fundamental polar vinyl monomers with non-polar monomers. Here in this chapter, general aspects on coordination-insertion of polar monomers will be discussed and the successful examples will be described later on.

6.4.1 General Aspects on Coordination-Insertion Polymerization of Polar Vinyl Monomers

Fundamental polar vinyl monomers, are expected to exhibit reactivities different from that of ethylene because electron-withdrawing or -donating groups are directly attached to the olefin moiety. The functional groups strongly influence the energies of the frontier molecular orbitals of the monomers, as indicated by the calculated orbital energy diagrams shown in Fig. 6.2 [10].

A prerequisite for the incorporation of vinyl monomers is π-coordination of an olefin double bond to a metal center. As far as electron-deficient metals are concerned, the energy of π(C=C), generally the HOMO level of the monomer, becomes an important factor in estimating the stability of the metal–olefin bond, because electron-donation from the C=C π bond to the empty d_σ orbital on the metal center is generally more dominant than back-donation from the metal d_π orbital to the empty C=C π* bond. As exemplified by Pd(II) α-diimine complexes, the more electron-deficient the monomer is (i.e., the lower the π-orbital of olefins is), the weaker the bonding to the metal is. This preference is opposite to that of electron-rich metals, where back-donation from the metal to the olefin's C=C π* orbital dominates for the formation of metal–olefin complexes.

In the case of polar vinyl monomers, competitive heteroatom σ-coordination over olefin π-coordination would constitute a serious problem (Fig. 6.3). AN prefers *N*-coordination to form the most stable σ-complex among the polar monomers, and MA and VAc follow. Vinyl chloride forms the weakest bond to the cationic Pd center via its chlorine atom among the monomers compared here.

For migratory insertion of polar monomers, regioselectivity (2, 1- or 1, 2-mode) plays an important role (Fig. 6.4). Thus far, with regard to insertion into Pd–alkyl bonds, electron-deficient monomers such as MA, VAc, and AN favor 2, 1-insertion and electron-rich monomers such as vinyl ethers prefer 1, 2-insertion (vide infra). Intrinsically, mono-substituted ethenes prefer 2, 1-insertion due to the steric repulsion between a migrating alkyl group and the substituent on the olefin [27]. This theory has been also accepted in the Mizoroki–Heck reaction, where the regioselectivity originates from the 2, 1- versus 1, 2-olefin insertion to an organopalladium intermediate [28, 29]. In addition, the energies required for the distortion of the monomers in insertion TS favor 2, 1-insertion. The steric repulsion between the ligand and the substituent on an olefin can affect the regioselectivity. The electronic effect (LUMO orbital ($2p_z$) coefficients of the sp^2 carbons and charge difference between the two sp^2 carbons) induced by substituents also modifies the selectivity (Fig. 6.4) Electron-rich vinyl ethers and propylene override the inherent 2, 1-insertion preference to undergo 1, 2-insertion due to their substantial electronic difference of two sp^2 carbons. In contrast, electron-deficient monomers have similar coefficients and charges on the two sp^2 carbons while the slight difference can strengthen 2, 1-selectivity.

There are several critical problems after the migratory insertion of polar monomers: (i) The resulting alkyl metal complexes can form strong chelates or

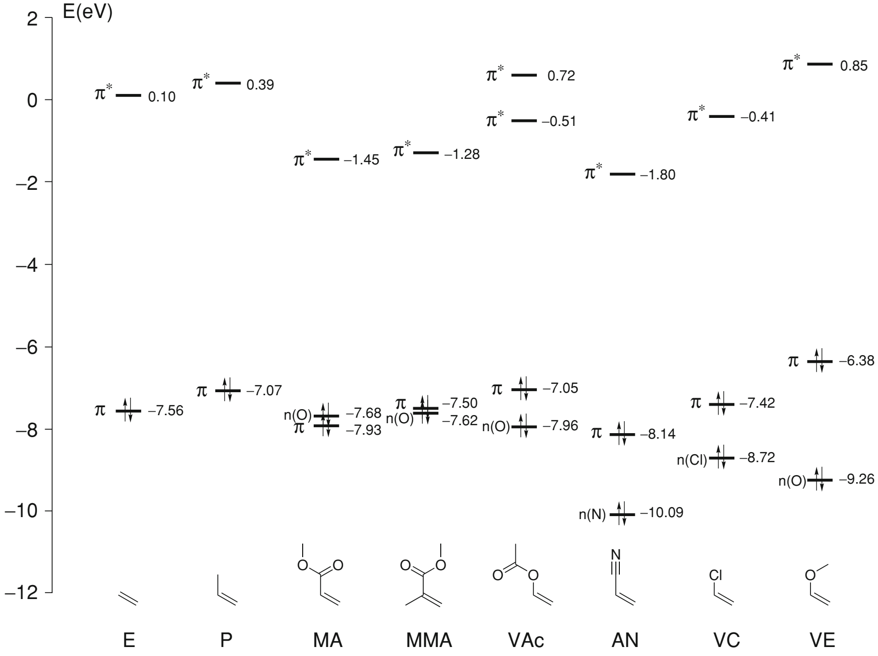
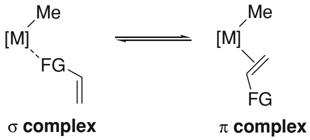


Fig. 6.2 Key molecular orbitals of the monomers described in this article as calculated by the B3LYP/6-311G(d,p) method

Fig. 6.3 σ- and π-coordination of polar vinyl monomers to a metal center



aggregates via the intra- or intermolecular coordination of polar groups to the metal center, which would prevent further coordination of the monomers. (ii) The polar substituents on the alkyl group of the intermediate, $L_nMCH(FG)CH_2R$, can dramatically change the reactivity of the subsequent insertion. (iii) For VAc, vinyl halides, and vinyl ethers, β-heteroatom elimination is also problematic if the polar groups (–OAc, –X (X=F, Cl, Br, I), –OR, respectively) are located at the β-position from the metal center.

6.4.2 Diimine/Pd or Ni Catalyst

In the mid-1990s, Brookhart et al. reported a series of olefin polymerization and copolymerization by cationic Pd(II) α-diimine complexes [5]. These catalysts were remarkably active for the copolymerization of non-polar olefins with polar vinyl

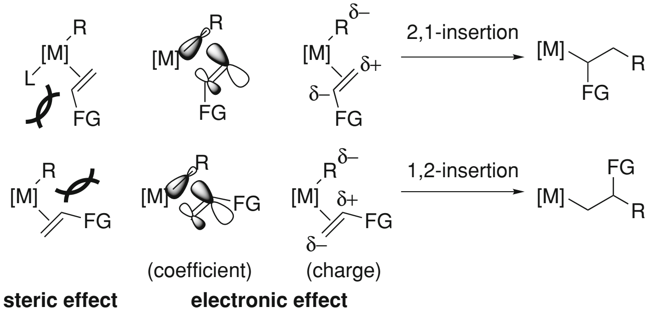
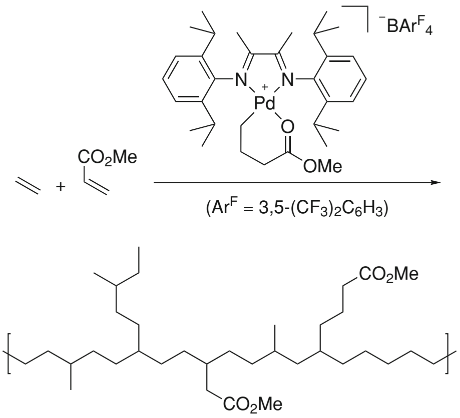


Fig. 6.4 The origin of regioselectivity in the insertion of polar vinyl monomers into metal–alkyl bonds

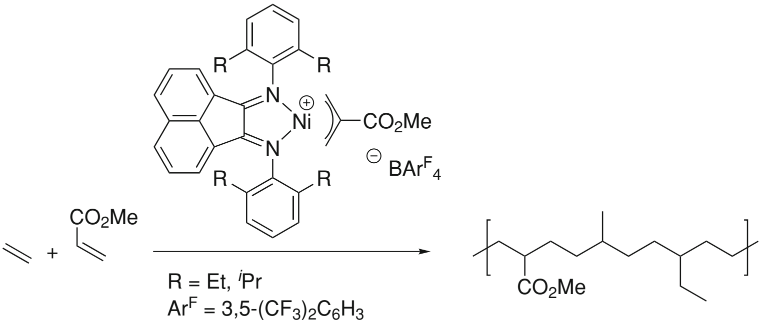
monomers such as acrylates [30, 31], methyl vinyl ketone [31], and silyl vinyl ethers [32] to yield highly branched copolymers (Scheme 6.6). By using Pd/diimine catalyst highly branched amorphous PE with acrylate units located predominantly at *branch ends*, rather than randomly incorporated in-chain, was obtained [30]. Nonetheless, other common monomers such as vinyl acetate, acrylonitrile, and vinyl chloride could not be copolymerized by these catalytic systems.

On the other hand, the copolymer produced by Ni/diimine catalyst is a linear (or branched, depending on the catalyst and reaction conditions) PE with *in-chain* acrylate incorporation (up to 1.33 mol %) as described in Scheme 6.7 [33, 34]. The copolymer given by phosphine-alkoxy Ni complexes possessed acrylate units both in-chain and chain-end (in ca1:1 ratio) into the substantially linear (none to a low degree of alkyl branching) PE backbone.

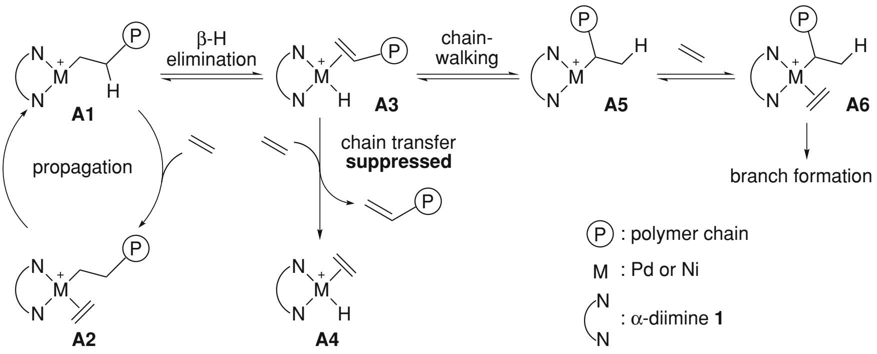
The origin of the chain structures whether linear or branched is explained by the mechanism drawn in Scheme 6.8. During chain propagation, β-agostic metal–alkyl intermediates (**A1**) can undergo a series of β-H elimination and reinsertion into the metal–hydride bond of **A3** in the opposite direction. When ethylene is incorporated after this isomerization, a methyl branch can be formed. Longer chain walks (isomerizations) introduce longer branches. This rapid β-hydride elimination from alkyl palladium and re-insertion of the eliminated C–C double bond to Pd-H, so-called chain-walking, is responsible for the formation of branched chains [30, 31, 35, 36]. The chain transfer is proposed to be slow in the α-diimine system both for Ni and Pd complexes so that high-molecular-weight of polyethylene is given. For Ni catalysts, dissociative and β-hydride transfer pathways were proposed to be the retarded process for the chain-transfer mechanism [37]. In the case of Pd catalysts, since olefin exchange proceeds via an associative pathway, the steric bulk in the axial sites of the square plane of these α-diimine complexes is a critical requirement for retarding the chain transfer [5].



Scheme 6.6 Copolymerization of ethylene with methyl acrylate catalyzed by cationic Pd α-diimine catalysts

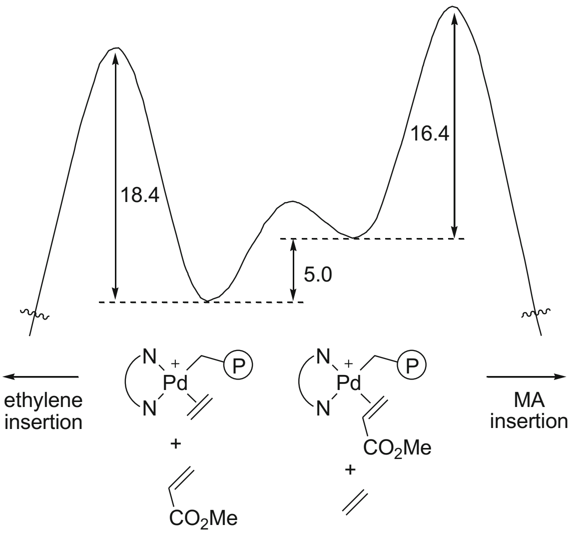


Scheme 6.7 Copolymerization of ethylene with MA catalyzed by Ni α-diimine complex



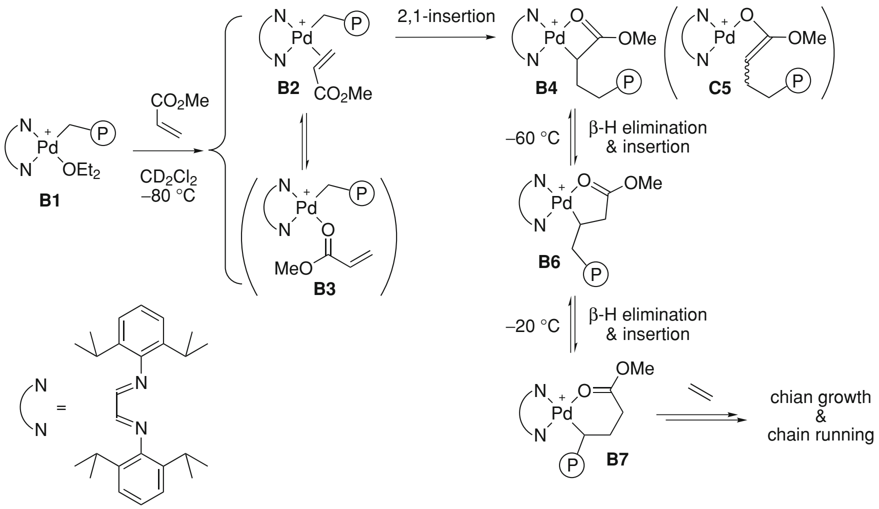
Scheme 6.8 Mechanism for ethylene polymerization and polymer branch formation with Pd and Ni α-diimine complexes

Fig. 6.5 Gibbs free energy (35 °C, kcal/mol) diagram calculated from Brookhart's kinetic experiments [30, 31]

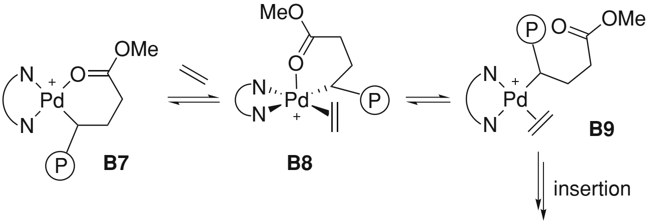


In Pd α-diimine complex-catalyzed copolymerization of ethylene and MA, the MA incorporation ratio increased with increasing the concentration of MA in the reaction solution; however, the copolymer molar masses and productivities significantly decreased [30, 31]. Although the migratory insertion of electron-deficient MA occurs much more rapidly than the insertion of non-polar olefins into a Pd–alkyl bond, this effect is overridden by the low binding affinity of MA to the electrophilic cationic metal center ($K_{\mathrm{MA/ethylene}} = 3 \times 10^{-4}$ at 35 °C). The Gibbs energy diagram for the insertion of comonomers is shown in Fig. 6.5. According to the Curtin–Hammet kinetics, ethylene insertion was more favorable than MA insertion.

The mechanism of the copolymerization of ethylene and MA catalyzed by Pd α-diimine complexes was confirmed by low-temperature NMR experiments as well as theoretical calculations [38–40] (Scheme 6.9). The complex **B2**, which is formed by the reaction of complex **B1** with MA, undergoes migratory insertion of MA into the Pd–alkyl bond in a 2, 1-mode with >95 % regioselectivity to form a four-membered chelate **B4**. The complex **B4** is believed to have a *C*-enolate structure of as opposed to an *O*-enolate structure (**B5**). The subsequent rapid β-H elimination and reinsertion leads to the formation of the most stable six-membered chelate **B7** via a five-membered chelate **B6**. In fact, MA insertion into the Pd–Me bond of {[N∼N]PdMe(OEt$_2$)} (BAr$^{\mathrm{F}}_4$) (Ar$^{\mathrm{F}}$ = 3, 5-(CF$_3$)$_2$C$_6$H$_3$) and rearrangements to the analogous structures of **B6** and **B7** were observed at –60 and –20 °C, respectively. Theoretical calculations have suggested that ethylene can be further incorporated not from the intermediates **B4** or **B6** but from **B7** because the overall barriers of ethylene insertion become minimum when of the reaction proceeds from **B7** through a two-step chelate-opening mechanism (Scheme 6.10). Both ethylene insertion and further β-H elimination/reinsertion can occur from **B7**,



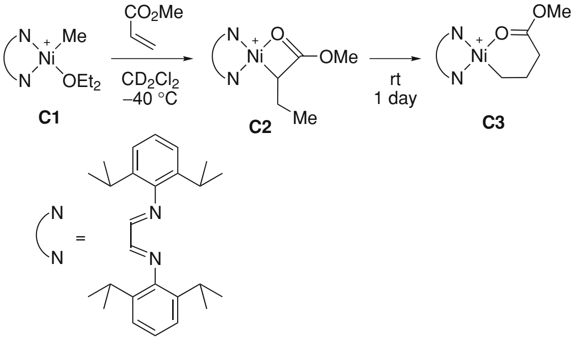
Scheme 6.9 Methyl acrylate insertion and rearrangements catalyzed by Pd α-diimine complexes



Scheme 6.10 Chelate-opening mechanism for ethylene coordination to complex **B7**

leading to the formation of a branched polyethylene with an ester group at the branch end. The intramolecular ester moiety strongly favors the chelate complex **B7** rather than the alkyl olefin species **B8** even under high ethylene pressure. Accordingly, the productivity of the copolymerization of ethylene and MA is generally lower than that of ethylene hompolymerization.

In the case of the Ni α-diimine catalyst, a four-membered chelate complex **C2** slowly rearranges at room temperature to a six-membered chelate complex **C3** within the course of 1 day while the rearrangement of the analogous Pd four-membered chelate complex occurs at −60 °C (Scheme 6.11). The harsh condition required for Ni catalyst compared to Pd and the slower chain-walking rate could be attributed to the higher stability of **C2** due to the higher oxophilicity of Ni.



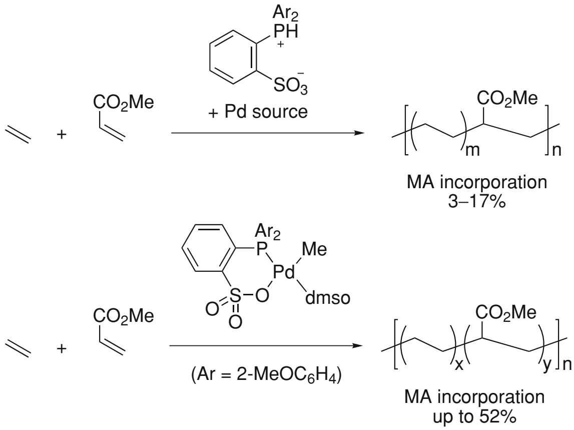
Scheme 6.11 Insertion of MA into {[N ~ N]NiMe(OEt$_2$)}(BAr$^F_4$) and the subsequent isomerization

6.4.3 Phosphine-Sulfonate/Pd Catalyst

Pd complexes bearing a phosphine–sulfonate ligand play an important role in the polymerization of polar vinyl monomers. The typical structure of the ligands reported to be effective for palladium-catalyzed coordination polymerization is $Ar_2P(C_6H_4$-*ortho*-$SO_3^-)$. In 1987, Murray at the Union Carbide Corporation first applied late transition metal complexes bearing phosphine–sulfonate ligands to ethylene oligomerization [41]. Since 1988, researchers at chemical companies including Shell (Drent, van Leeuwen et al.) [42, 43], later in Rohm and Haas (Goodall et al.) [44–48], and others [49–52] have filed several patents for polymerization processes using phosphine–sulfonate ligands. Immediately after the first academic reports in 2002, [43] these catalysts have attracted considerable attention from a wide range of research groups.

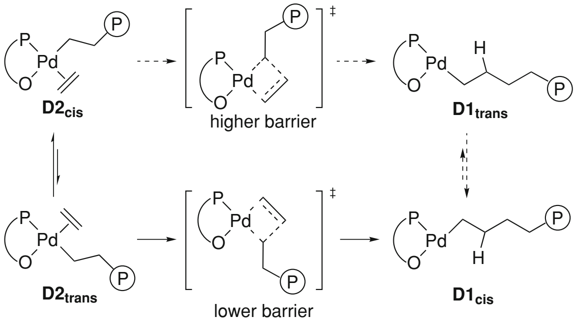
The copolymerization of E/MA catalyzed by Pd phosphine–sulfonate system provides highly linear ethylene/alkyl acrylate copolymers with in-chain acrylate incorporation (Scheme 6.12) [43]. The structure of the copolymer was unambiguously determined by NMR analyses, in which the number of Me branches on the backbone of the copolymer was very low (ca. 1 Me per 1,000 carbons) and the incorporation ratio of MA was ca. 10 %. No double acrylate insertions were observed even in the copolymer produced under high concentration of MA.

One of the key characteristics of Pd phosphine–sulfonate polymerization catalysts is the ability to produce highly linear polyethylenes. The mechanism of ethylene homopolymerization catalyzed by the Pd phosphine–sulfonate system was theoretically investigated by using DFT calculations [53, 54]. Because of the unsymmetrical nature of phosphine–sulfonate ligands, both cis and trans isomers should be considered in their square planar metal complexes. In Schemes 6.13 and 6.14, the isomers of the alkyl group or hydride located at the cis position of the phosphorous atom are described as “cis” and vice versa. It has been confirmed by X-ray crystallographic analyses that the alkyl chain is located at the cis to the



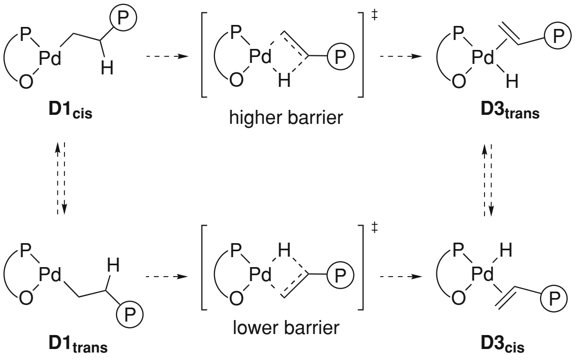
Scheme 6.12 Copolymerization of ethylene with MA catalyzed by Pd phosphine–sulfonate system

Scheme 6.13 Ethylene insertion catalyzed by Pd phosphine–sulfonate complexes

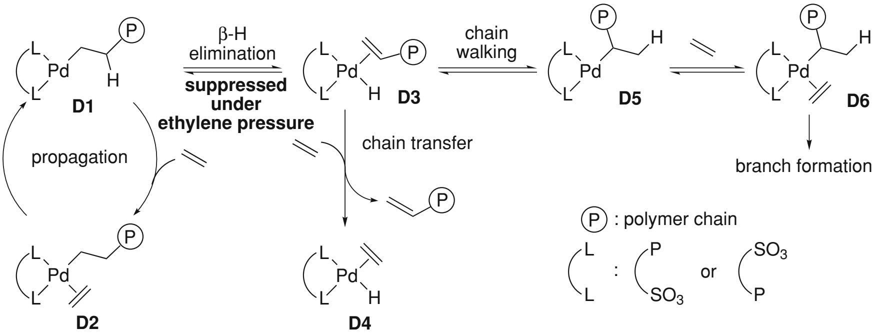


phosphorous atom in the more stable isomer. This is because the strong trans influence of the phosphorous atom does not favor the existence of an alkyl chain trans to the phosphorous atom. In contrast, ethylene insertion occurs with a lower barrier from the isomer **D2**$_{\mathbf{trans}}$. In this case, the migrating ability of the alkyl chain is enhanced due to the strong trans effect of the phosphorous atom leading to facile migratory insertion of ethylene. It should be noted that the olefin can accept a strong back-donation from Pd because of the charge of the metal center and the nature of the sulfonate located at the trans position (i.e., weak σ-donor and weak π-acceptor).

Similarly, β-H elimination from the alkylpalladium complexes could proceed both from **D1**$_{\mathbf{cis}}$ and **D1**$_{\mathbf{trans}}$ isomers (Scheme 6.14) [54]. The trans isomer, **D1**$_{\mathbf{trans}}$, is much more susceptible to β-H elimination reaction than **D1**$_{\mathbf{cis}}$. The transition state of β-H elimination from **D1**$_{\mathbf{trans}}$ is lower in energy than that of ethylene insertion from **D2**$_{\mathbf{trans}}$. Nevertheless, it was found that all the routes to reach **D1**$_{\mathbf{trans}}$ require as high energy as ethylene insertion. On the other hand, the β-H



Scheme 6.14 β-H elimination catalyzed by Pd phosphine–sulfonate complexes



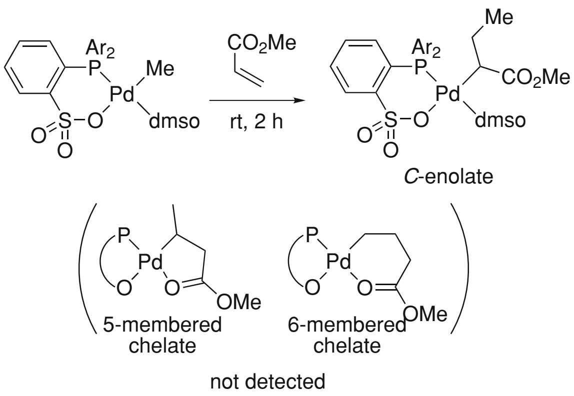
Scheme 6.15 Mechanism for ethylene polymerization and linear polyethylene formation with Pd phosphine–sulfonate complexes

elimination pathway from $\mathbf{D1_{cis}}$ requires as high energy as the ethylene insertion from $\mathbf{D2_{trans}}$. Thus, the barriers for (i) ethylene insertion from $\mathbf{D2_{trans}}$, (ii) β-H elimination from $\mathbf{D1_{cis}}$, and (iii) the routes to $\mathbf{D1_{trans}}$ are comparable in energy. This result suggests that, the insertion of ethylene (i) should be the most favorable route *in the presence of ethylene*, because high concentration of ethylene accelerates only the route (i).

As summarized in Scheme 6.15, Pd phosphine–sulfonate systems produce linear polyethylene because β-H elimination is suppressed *under the ethylene pressure*. It should be noted that this catalytic system can undergo β-H elimination *in the absence of ethylene*. If $\mathbf{D3_{trans}}$ or $\mathbf{D3_{cis}}$ once form by β-H elimination.

The mechanism of the copolymerization of ethylene with MA catalyzed by Pd phosphine–sulfonate systems has been investigated experimentally and theoretically. Mecking et al. have found that the 2, 1-insertion of methyl acrylate into the Pd–Me bond of affords Pd *C*-enolate complex (Scheme 6.16) [55]. Whereas the corresponding *C*-enolate of the cationic Pd α-diimine complexes rapidly isomerizes at −60 °C, the *C*-enolate of the phosphine-sulfonate containing the fourth

Scheme 6.16 Insertion of MA into [P ~ SO_3]PdMe(dmso)



ligand DMSO was particularly stable. Given that the five-membered β-metallochelate is the most stable structure in the absence of any additional ligand [53], the fourth ligand may play an essential role in stabilizing intermediate *C*-enolate rather than the five- or six-membered chelate structures. The analysis of the polymer structures revealed that the subsequent ethylene insertion occurred not into the *C*-enolate before chain-walking.

The Pd phosphine–sulfonate catalyst was found to be applicable to the copolymerization of ethylene with various comonomers, including acrylates [42, 43, 55–57], vinyl acetate [58], allyl acetate [59], allyl alcohol [59], acrylonitrile [60], vinyl fluoride [61], alkyl vinyl ethers [62], vinyl ketones [63], *N*-vinyl-2-pyrrolidinone [64], acrylamides [64], *N*-vinylcarbazole [64], *N*-vinylphthalimide [64], and functionalized norbornene derivatives (Scheme 6.17) [65].

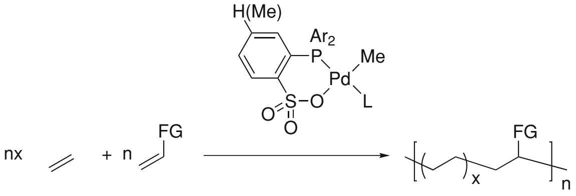
Ni phosphine–sulfonate complexes have also been synthesized and applied to ethylene homopolymerization to afford linear polyethylenes (1–18 branches per 1,000 carbons) [55]. In contrast to the Pd catalysts, however, Ni phosphine–sulfonate complexes have not yet been reported to be active for the copolymerization of fundamental polar monomers.

Although the phosphine–sulfonate ligands had been the sole class of ligand applicable to the synthesis of linear functionalized polyethylene, another example, bisphosphine monoxide (BPMO), was recently reported to be an effective ligand for Pd-catalyzed copolymerization of ethylene and polar vinyl monomers to form linear random copolymer [66].

6.5 Copolymerization of Polar Monomers with Other Monomers

Copolymerization of polar vinyl monomers with carbon monoxide is briefly summarized in this section. Since the first discovery of the copolymerization of ethylene and carbon monoxide in 1951 [67], a variety of palladium catalysts with

Scheme 6.17 Pd phosphine–sulfonate catalyzed copolymerization of polar monomers with E to form functionalized polyethylene



FG = COOMe, CN, OAc, OR, F, COMe, CONH^{i}Pr, NC(=O)$(CH_2)_3$
CH$_2$OH, CH$_2$NHBoc, CH$_2$OAc,

Ar = 2-OMe-C_6H_4, Ph, ^{i}Pr, *cyclo*-Hex
L = pyridine, 2,6-lutidine, DMSO

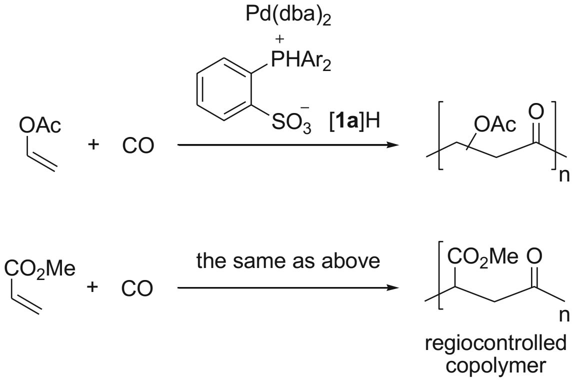
bidentate ligands have been developed for the effective copolymerization of olefins with CO. Currently, the catalytic systems most frequently used for ethylene/CO copolymerization, propylene/CO copolymerization, ethylene/propylene/CO terpolymerization, and propylene/CO copolymerization are palladium complexes of the type $[Pd(L^\wedge L')(S)_2][X]_2$, where $L^\wedge L'$ ($L = \text{or} \neq L'$) is a *cis*-chelating bisphosphine ligand such as 1, 3-bis(diphenylphosphino)propane (DPPP), S is a solvent molecule, and X is an anion with low coordination capability. Additionally, an oxidant is often added to the reaction systems in order to minimize the formation of inactive reduced palladium species [68, 69]. On the other hand, for styrene/CO copolymerization or for ethylene/styrene/CO terpolymerization, bis-sp^2-nitrogen ligands, such as 2, 2′-bipyridine (BPY), 1, 10-phenathroline (PHEN), or α-diimines, are suitable as the $L^\wedge L'$ in $[Pd(L^\wedge L')(S)_2][X]_2$ [68, 69].

In contrast to that functionalized styrene or 1-alkenes were applicable to the copolymerization with CO, the copolymerization of polar vinyl monomers with CO remained as an unsolved problem until very recently.

In 2007, the alternating copolymerization of vinyl acetate (VAc) with CO was accomplished using a mixture of Pd(dba)$_2$ and phosphonium–sulfonate as a catalyst (Scheme 6.18, top) [70]. The alternating structure of the obtained copolymers was unambiguously confirmed by NMR analyses and MALDI-TOF mass analysis. However, head-to-tail selectivity was found to be less controlled, which suggests that VAc insertion into the acyl–palladium bond may occur in both the 2, 1- and 1, 2-mode. The productivity was up to 3.0 g mmol^{-1} h^{-1} and the molecular weight (M_n) was up to 38,000.

The alternating copolymerization of methyl acrylate (MA) with CO was also accomplished by using the same catalytic system (Scheme 6.18, bottom) [71, 72]. The activity of MA/CO copolymerization (up to 4.4 g mmol^{-1} h^{-1}) and the molecular weight (up to $M_n = 30{,}000$) of the copolymers were similar to those in the case of VAc/CO copolymerization. The NMR studies revealed that the regiochemistry is strictly regulated, implying that the insertion of MA into the acyl–palladium bond occurs only in the 2, 1-insertion mode.

Scheme 6.18 The alternating copolymerization of polar vinyl monomers with CO



6.6 Conclusions and Outlook

In this chapter, two types of coordination polymerization of polar vinyl monomers, namely, early-transitionmetal catalyzed coordinateon-addition polymerization and late-transitionmetal catalyzed coordination-insertion polymerization were reviewed. By the former method, homopolymer of polar vinyl monomers and polyethylene/poly polar monomer block copolymers were produced. Contrastively, random incorporation of polar monomers to polyethylene was accomplished by the latter method. Thus, both of these methods are complementary and will be further studied in parallel. .

The polymeric materials obtained here are highly attractive from the industrial viewpoint; however, the catalytic activities that have thus far been achieved are not sufficient for industrialization. Therefore, one of the most important objectives is the improvement of catalytic activity for the copolymerization of fundamental polar monomers. Today's economical and environmental concerns induce another requirement for this chemistry. Despite the remarkable progress described in this chapter, most methods have been based on the use of rare metals as a catalyst. Thus, the replacement of such a metal by less expensive and ubiquitous metals such as iron and titanium constitutes significant future challenges. Alongside further progress regarding the catalysts, the physical and chemical properties of the new materials will be extensively investigated, since the potential performance of them has not yet been completely revealed.

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Chapter 7
Metathesis and Polymerization

Kohtaro Osakada

Abstract This article reviews olefin metathesis, its history, use of heterogeneous and well-defined molecular catalysts, mechanism related to organometallic chemistry and application of the reactions. Group VI and VIII transition metal catalysts are the most common in the olefin metathesis, although several other transition metal compounds also catalyze the reaction. The olefin metathesis is used in the ring-opening polymerization of the strained cyclic olefins, while acyclic unsaturated molecules can also be adopted as the monomer of the polymerization, and the substrate for the ring-closing metathesis or cross metathesis reactions. Application of the olefin metathesis is extended to synthesis of the new functionalized polymers, organometallic compounds, organic compounds from marine animals, and interlocked molecular systems.

7.1 Introduction

Olefin metathesis reaction involves mutual exchange of the carbon-carbon double bonds catalyzed by transition metal complexes, as shown in Scheme 7.1. It causes cleavage of the two C=C double bonds and formation of new C=C double bonds under mild conditions.

Historical background of the olefin metathesis is quite exciting to the scientists of organometallic, macromolecular, organic, and catalytic chemistry. The olefin metathesis was discovered during the study of olefin polymerization using Ziegler-Natta type catalysts [1]. Eleuterio in DuPont Co. conducted the study on the Mo-based catalysts for propylene polymerization, and found the formation of the polymer containing ethylene units in the polymer chain. It was ascribed to the

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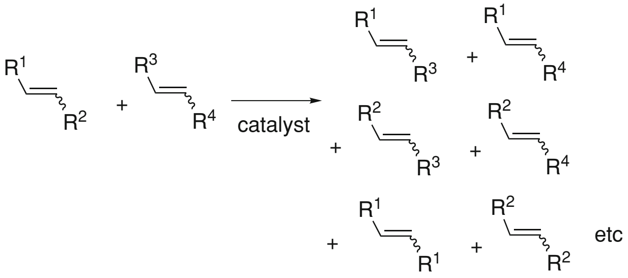


Scheme 7.1 Olefin metathesis

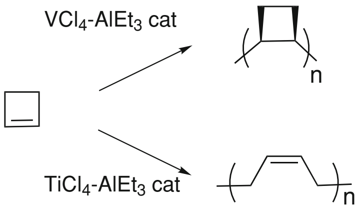
metathesis of propylene, giving ethylene and 2-butene, during the polymerization. Another productive olefin metathesis reaction was found also during the study of polymer synthesis. Cyclobutene undergoes vinyl polymerization in the presence of VCl_4–$AlEt_3$ catalyst, similar to many other cyclic olefins with ring strain [2, 3]. The product contains four-membered cyclic group in every repeating unit. Use of $TiCl_4$–$AlEt_3$ catalyst, however, afforded the polymer with the C=C double bonds and without a ring structure, as shown in Scheme 7.2 [4]. The polymer attracted attention because of its *cis*-rich polybutadiene structure and the rubbery properties.

Calderon summarized these apparently different reactions promoted by various transition metal catalysts and concluded that all the reactions proceed by exchange of the alkylidene groups (=CRR’) rather than transalkylation [5]. He also named them as olefin metathesis, although the other ones, such as olefin disproportionation, had been proposed by other research groups.

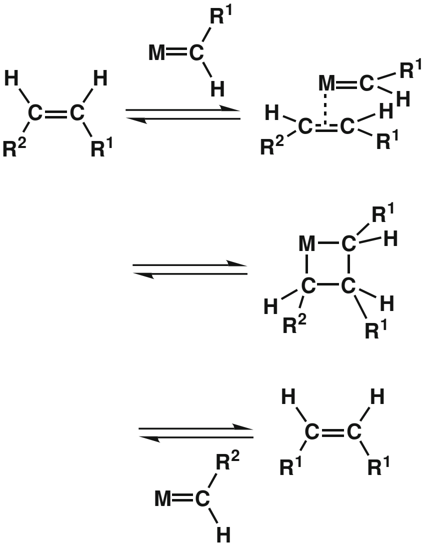
The mechanism of this novel reactions had been under discussion by several research groups, and the final mechanism was proposed by Hérisson and Chauvin in 1971, which involves organometallic intermediates [6]. Their proposed mechanism is summarized in Scheme 7.3. The intermediates having a carbene ligand are generated upon mixing the transition metal compounds and the alkylaluminum. Addition of a C=C double bond to the metal-carbene bond yields the metallacyclobutane having a four-membered ring, and elimination of the olefin product regenerates the new carbene-transition metal complexes. Structures of the products of the olefin metathesis and ring-opening metathesis polymerization are consistent with those based on the mechanism. The apparently reversible mechanism explains results of the olefin metathesis reactions. The multicomponent catalysts composed of transition metal salts, basically of Mo and W, and alkylaluminum, were employed in a number of the reactions.

Study of the transition metal complexes with carbenoid or metallacyclobutane structures were directed toward the clarification of the reaction mechanism. Although the transition metal complexes with carbene ligands were isolated, many of them prepared in the initial period did not promote the olefin metathesis reactions, efficiently. Casey prepared the tungsten complex with a diphenylcarbene

Scheme 7.2 Polymerization of cyclobutene



Scheme 7.3 Mechanism of olefin metathesis



ligand, W(=CPh$_2$)(CO)$_5$, starting from a "Fischer type" complex, W(=CPh(OMe))(CO)$_5$, and found that the reaction of olefin with the complex yielded the products of the stoichiometric metathesis reaction [7, 8]. Katz employed the complex as the catalyst of metathesis of isotope-labelled 1-olefins and obtained all the products expected from the olefin metathesis reaction [9].

The olefin metathesis has advantages in a variety of the catalysts, which enabled choice of the best catalyst for each reaction, high atomic economy, and mild reaction conditions. Ring-opening polymerization of the olefins equipped with four- and five-membered rings and with strained multicyclic ring systems proceeds smoothly to yield the corresponding polymers owing to higher stability of the products. Strained structures of the monomers served to the smooth reaction, which is accompanied by release of the ring strain. Although the olefin metathesis reaction occurs reversibly, discovery of the highly active catalyst during these decades enabled the selective reactions of the less strained or unstrained substrates. Ring-closing metathesis of terminal dienes and cross-metathesis of two terminal olefins convert the substrates to the cyclic or acyclic products easily when the reaction system is designed to release gaseous ethylene product from the reaction mixture. Selectivity of the reactions, including *E*/*Z* selectivity and enantioselectivity of the products, has been improved by design of the new molecular catalysts.

The following sections describe the representative catalysts and reactions and recent application of the olefin metathesis.

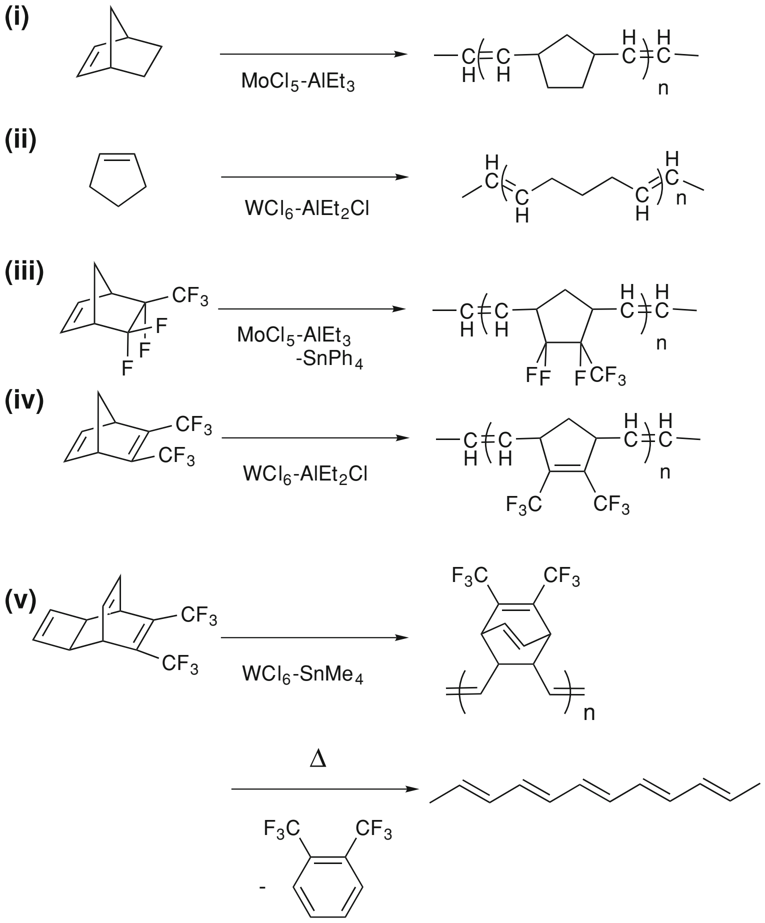
7.2 Catalysts

7.2.1 Multicomponent Catalysts

The initial olefin metathesis catalysts were mostly the heterogeneous ones similar to the Ziegler-Natta type catalysts, as mentioned in the previous section. Norbornene, having a bicyclic structure, undergoes ring-opening metathesis polymerization in the presence of the two component catalysts, transition metal salts and alkylaluminum. $TiCl_4$–$LiAlH_4$ catalyst also promotes the reaction of norbornene derivatives [10]. Chlorides of many transition metals, such as Ti, Zr, V, Mo, and W, catalyze the ring-opening polymerization of cyclopentene and cycloheptene in the presence of $AlEt_2X$ ($X = Et$, Cl) (Scheme 7.4i, ii) [11].

Norbornenes with fluorinated substituents undergo the smooth reaction catalyzed by a WCl_6–$AlEt_2Cl$ mixture to produce the fluorinated polymers (Scheme 7.4iii, iv) [12, 13]. Feast designed the multicyclic monomers with ring strain and conducted the ring-opening polymerization to obtain the polymers having a fluorinated multicyclic group in every structural unit (Scheme 7.4v) [14, 15]. Each repeating unit undergoes thermally induced retro-Diels-Alder reactions to produce the polyacetylene accompanied by elimination of the fluorinated aromatic compound. Since the precursor polymer of polyacetylene are soluble, their molecular weight and the molecular weight of the resulted polyacetylene can be estimated. Physical properties of the polyacetylene obtained by this method were investigated by using spectroscopies and X-ray diffraction, and compared with that obtained from acetylene using Shirakawa's method [16, 17].

The reactions using the heterogenous catalysts still have importance in industrial process. The reactions and catalysis in the industry are surveyed in the recent review articles [18, 19]. Two-component catalysts have been employed in the polymer synthesis in an industrial scale. In addition to the cocatalysts, organotin compounds or transition metal salts are also added as the third component of the catalysts. It is used in the ring-opening polymerization of norbornene and other cyclic olefins to form the tough and flexible polymer material in a molded shape. The heterogeneous catalysts for olefin polymerization are obtained by using the metal oxides as the support. Re(VII) oxide supported on alumina and Mo(VI) oxide supported on silica are the common heterogeneous catalysts for olefin metathesis.



Scheme 7.4 Ring-opening metathesis polymerization by Mo and W catalysts

7.2.2 Homogeneous Catalysts

The heterogeneous catalysts for olefin metathesis, composed of the transition metal salts and alkylating reagents, are highly active. Although the initial molecular catalysts showed much lower activity than the heterogeneous ones, the new molecular catalysts, alkylidene complexes of Mo and Ru, in particular, improved their performance and enabled the reactions which had not been realized by the conventional heterogeneous catalysts.

Several heterogeneous catalysts still show higher activity than those using most molecular catalysts. The ring-opening metathesis polymerization of cyclic olefins catalyzed by molecular transition metal complexes, however, has advantage in regulation of molecular weights of the products. Stereoselective polymerization of norbornene derivatives was also achieved. Introduction of chiral substituents on the ligand of the complexes induced chirality to the products, polymers and organic compounds.

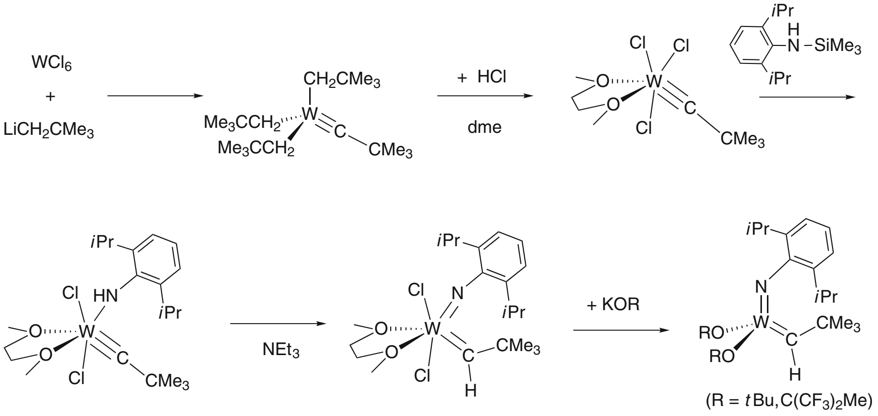
A number of books and reviews on the olefin metathesis using molecular catalysts are available [20–29]. In this section, representative catalysts and their reactions are briefly mentioned, and recent application of the olefin metathesis is summarized in the next section.

7.2.2.1 Mo and W Catalysts

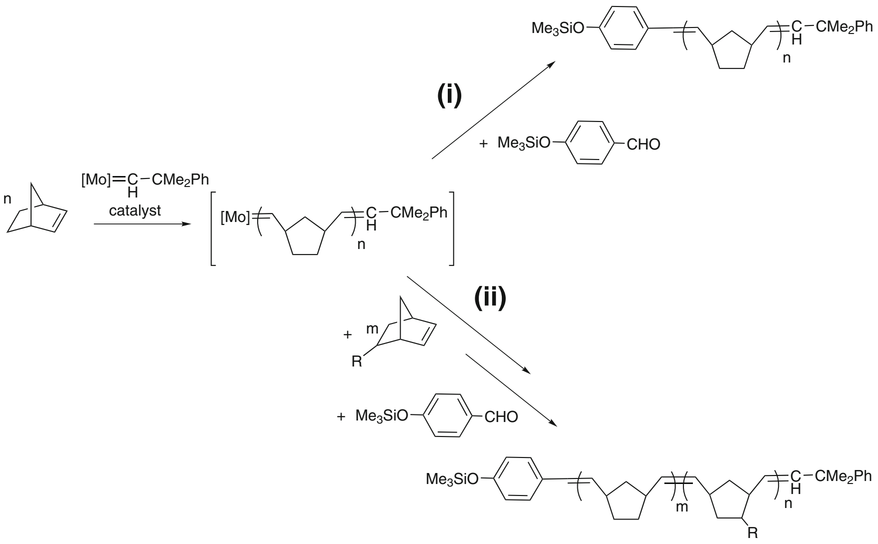
The proposal of the mechanism for the olefin metathesis prompted the studies on the synthesis of alkylidene (substituted carbene)-transition metal complexes as well as their reactions towards olefins. Schrock succeeded in synthesis of Ta and Nb complexes with neopentilydene ligands from α-hydrogen elimination reaction of the neopentyl complexes [30]. Tungsten complex with a neopentilydiene ligand, $WCl_2(=O)(=CHCMe_3)(PEt_3)_2$, was obtained by transmetalation of the alkylidene ligand of the Ta complex and catalyzed metathesis of inner olefins in the presence of $AlCl_3$ cocatalyst.

The well-defined molecular catalyst, $W(OR)_2(=CHCMe_3)(=N(2,6\text{-}(i\text{Pr})_2C_6H_3))$ ($R = t\text{Bu}, C(CF_3)_2Me$), was obtained by the procedure shown in Scheme 7.5 [31, 32]. These complexes exhibit high catalytic activity for the ring-opening metathesis polymerization, the ring-closing metathesis, and cross-metathesis reactions without using a cocatalyst. Bulky arylimide and alkoxide ligands are introduced to the complex. Although the complex contains tetra-coordinate metal center, the sterically bulky ligands stabilize the metal center and prevent the molecule from undesired dimerization. The alkoxide ligands with electron-withdrawing CF_3 groups lower the LUMO level of the complex and make coordination of the olefin substrate easy.

The Mo analogues are obtained in a similar manner, and exhibit higher catalytic activity than the W catalyst. One of the striking features of the Mo catalyst is living ring-opening polymerization of the cyclic olefins, as shown in Scheme 7.6 [33–35]. The reaction is initiated by addition of the C=C bond of norbornene to the Mo=C bond and cleavage of the resulted four-membered metallacycle. The yielded cyclopentylmethylidene-Mo compound undergoes repeated reactions with norbornene to cause polymer growth. Quenching of the growing polymer end with aromatic aldehydes results in the polymers having terminal CMe_2Ph group, derived from the initiator, and the aromatic end group (Scheme 7.6i). The terminal structure of the polymer indicates that the growing polymer end has the alkylidene =Mo bond, which undergoes Wittig-type coupling with the aldehydes. Molecular weight and polydispersity of the polymer are consistent with the living polymerization with quantitative efficiency of the Mo-containing initiator. Synthesis of AB type block copolymer from the two norbornene derivatives with different substituents was also noted (Scheme 7.6ii). Thus, the polymerization system has advantages in productivity, control of molecular weights, block copolymer



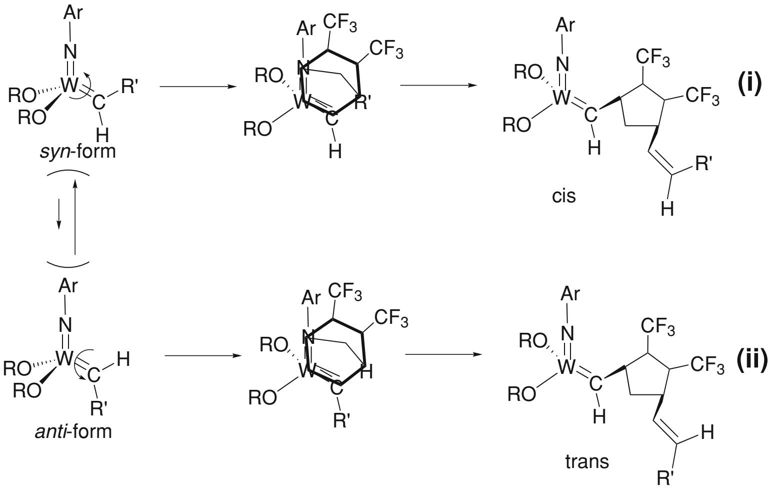
Scheme 7.5 Synthesis of W-alkylidene complex



Scheme 7.6 Ring-opening metathesis polymerization catalyzed by Mo-alkylidene complexes

formation, and functionalization of the terminal groups. High sensitivity of the catalyst to oxygen and water, however, makes purification of the substrates and the solvent, and handling the catalyst under air- and moisture-free conditions required.

The catalyst in Scheme 7.5 has a symmetrical structure owing to the almost linear M–O–C and M–O–N bonds. Thus, *syn* and anti structures around the



Scheme 7.7 Stereoselective ring-opening metathesis polymerization of norbornene

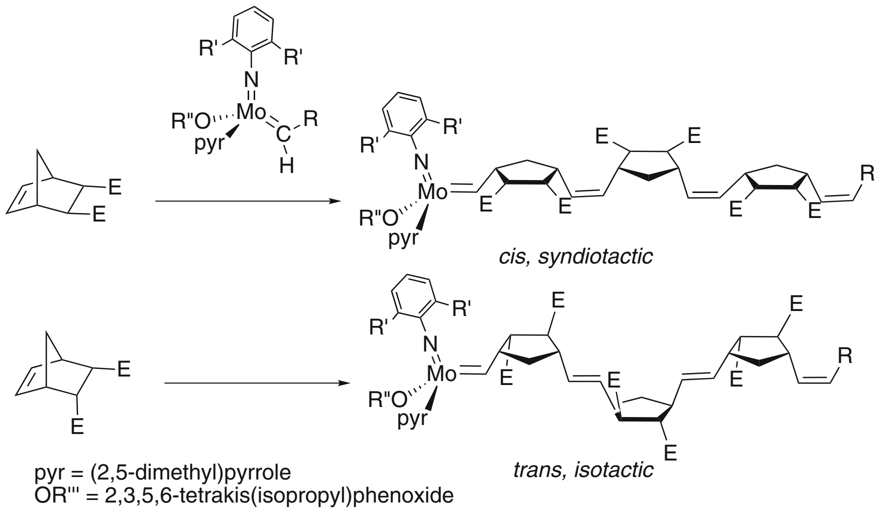
alkylidene=Mo bond (Scheme 7.7) influence the stereochemistry of the reaction with the olefin substrates. Addition of *exo,exo*-disubstituted norbornene to the stable syn-alkylidene-Mo complex results in the linkage of *cis*-vinylene group between the five-membered rings (Scheme 7.7i).

The polymer structures are regulated strictly by using recent Mo catalysts. The *exo,exo*-norbornene derivatives are converted to the polymer having a *cis*,syndiotactic structure as shown in Scheme 7.8 [36–38]. *Exo,end*-norbornene monomer produces the polymer having *trans*,isotactic structures along the polymer chain.

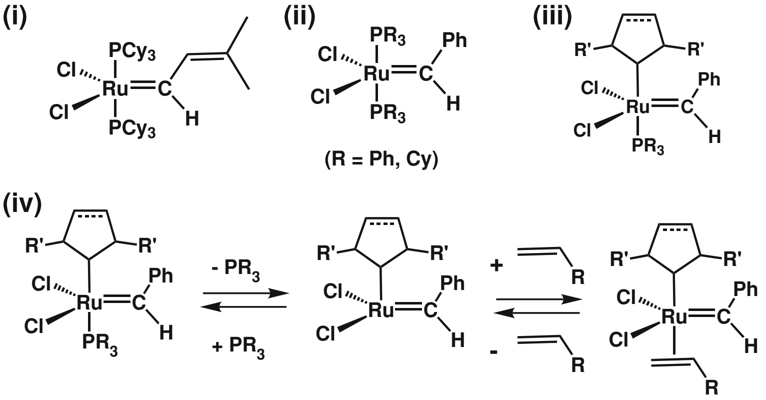
7.2.2.2 Ru Catalysts

$RuCl_3$ was known to catalyze the ring-opening polymerization of norbornene in polar solvents such as BuOH, which was applied to the polymer synthesis in an industrial scale [18]. Ru(II)-phosphine complexes, such as $RuCl_2(PPh_3)_3$, catalyze metathesis of silyl ethenes [39–41]. Addition of organosilanes having an Si–H bond or reducting agents such as $NaBH_4$ to the reaction mixture is required to make the reaction smooth.

$[Ru(H_2O)_6](Tos)_2$ was found to catalyze the ring opening polymerization of the functionalized norbornene without addition of a cocatalyst [42]. The catalyst is easy to prepare and works efficiently even in aqueous media. The first well-defined molecular Ru catalysts that do not require cocatalyst were discovered in the line of this study; the Ru complex with a vinylmethylidene ligand (Scheme 7.9i) was obtained from the reaction of dimethylcyclopropene with $RuCl_3$ and the resulted complex catalyzes the olefin metathesis. Further studies led to discovery of the



Scheme 7.8 *Cis*- and *trans*-polymers of norbornene



Scheme 7.9 Ru catalysts for olefin metathesis (**i–iii**) and their activation process (**iv**)

well-refined metathesis catalysts, $RuCl_2(=CHPh)(PR_3)_2$ (R = Ph, Cy) (Scheme 7.9ii) [43, 44]. Replacement of a phosphine of the above complexes with an NHC (*N*-heterocyclic carbene) ligand provides the molecular catalyst with a higher activity (Scheme 7.9iii) [45]. These two complexes are known as the first- and second-generation Grubbs catalysts, respectively. The benzylidene ligand of the complexes reacts with the olefin substrate at the initial stage of the reaction, while the alkylidene-Ru species formed by the olefin metathesis has a similar coordination structure and resumes the metathesis reaction. High activity of the NHC-containing catalyst is attributed to facile dissociation of the phosphine ligand at the *trans* position of the NHC, as shown in (iv) [46–48]. Highly electron-donating

NHC ligand activates the Ru–P bond, but does not influence the Ru-olefin bond. Thus, olefin coordination to the Ru center is facilitated by the NHC ligand, which results in high catalytic activity for the reaction. The first-generation Grubbs catalyst, after the reaction, can be removed from the organic product by addition of $P(CH_2OH)_3$ to the reaction mixture and extraction of the Ru catalyst residue bonded with the water-soluble phosphine ligands [49].

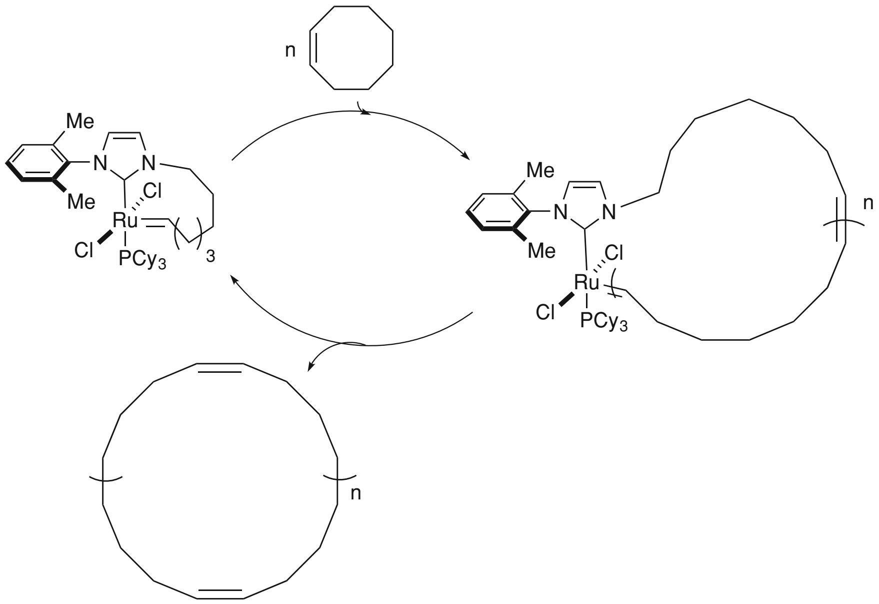
The above Ru complexes catalyze ring-opening polymerization of not only norbornene derivatives but also less-strained cyclic olefins such as cyclooctene [50–52]. The product of the ring-opening polymerization of cyclooctene is the hydrocarbon polymer composed of the eight carbon repeating units having a C=C bond, while the reaction of cyclooctatetraene derivatives produces the substituted polyacetylenes. Grubbs designed the Ru catalyst with the NHC ligand whose nitrogen atom is connected to the coordinating carbene carbon through an oligomethylene spacer (Scheme 7.10). Ring-opening polymerization of cyclooctene catalyzed by the complex afforded the species having a ruthenacycle with a large ring structure [53–55]. The ring-opening polymerization was applied to the other monomers, and substituted norbornene is converted to the macrocyclic polymer with high molecular weight, and a single molecule of the polymer was analyzed by AFM technique [56].

This catalysis provides synthesis of the macrocyclic polymer with regulated molecular weights, which is of interest because of the expected physical properties of the cyclic polymer different from the corresponding linear polymers. Only a few reports have appeared on the macrocyclic polymer with regulated molecular weights until very recently [57–59].

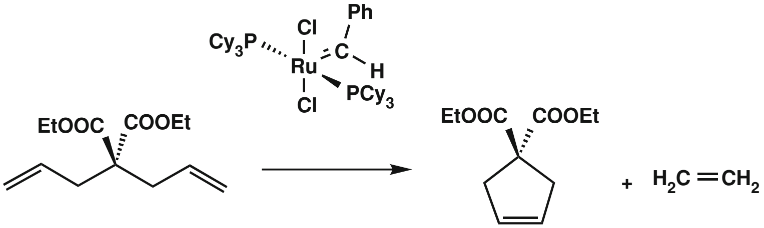
The olefin metathesis reactions which are quite important in their application are ring-closing metathesis of terminal dienes. The catalysts are active for various substrates, and form the complexes from five-membered rings to macrocyclic compounds. The catalysts are not influenced by functional groups in the molecules of the starting compounds. 1,6-Hexadiene with COOEt groups, for example, undergoes smooth ring-closing metathesis reaction to produce the cyclopentene having the functional groups (Scheme 7.11). The reaction is closely related to the application of the olefin metathesis which is mentioned in Sect. 7.3.

7.2.2.3 Molecular Catalysts Using Other Transition Metals

Rhenium is among the central metals used in the heterogeneous catalysts for the olefin metathesis reactions [60], similar to Mo, W, and Ru. Penta-coordinated alkylidene Re complexes with the bulky auxiliary arylimide ligand catalyze the reaction in the presence of Lewis-acid cocatalysts such as $AlCl_3$ and $GaCl_3$ [61]. A bulky alkylidyne ligand forms the tetrahedral complex (Scheme 7.12i) which is isoelectronic to the highly catalytically active imido(alkylidene)molybdenum complex (ii) [62–64]. The complex with two $OC(CF_3)_2Me$ ligands catalyzes the metathesis of inner olefins.



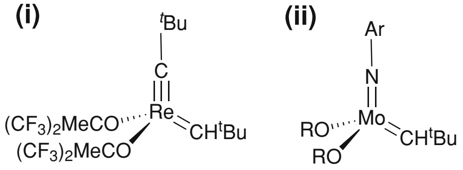
Scheme 7.10 Synthesis of cyclic poly(cyclooctene)



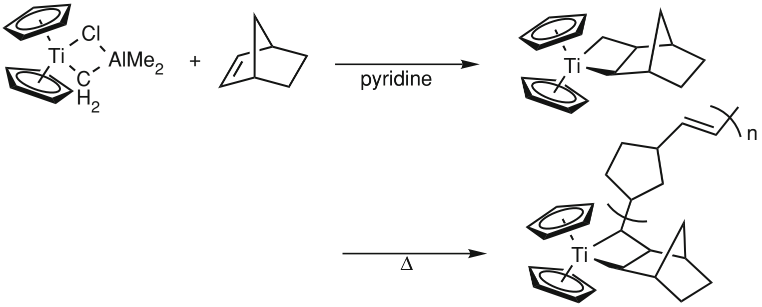
Scheme 7.11 Ring-closing olefin metathesis

The complex with alkyl, alkylidene, and alkylidyne ligands on the Re center also catalyzes metathesis of inner olefins, although the catalytic activity is not stable at high temperature or after a long reaction period [65]. Rhenium complex having an oxo (=O) ligand shows a moderate catalytic activity in the presence of $GaBr_3$ cocatalyst [66]. Fixation of the Re catalyst on the silica surface provided the olefin metathesis catalyst with high activity [67].

Although Ti is one of the first transition metals used as the catalyst in the presence of alkylaluminum cocatalysts, the activity of the isolated complex with a Ti=C bond was not high [68]. The adduct of $AlMe_2Cl$ to the methylene-titanium complex, Tebbe reagent [69], was converted to titanacyclobutane upon the reaction with norbornene in the presence of pyridine or dimethylaminopyridine [70].



Scheme 7.12 Ru- and Mo-alkylidene catalysts for olefin polymerization

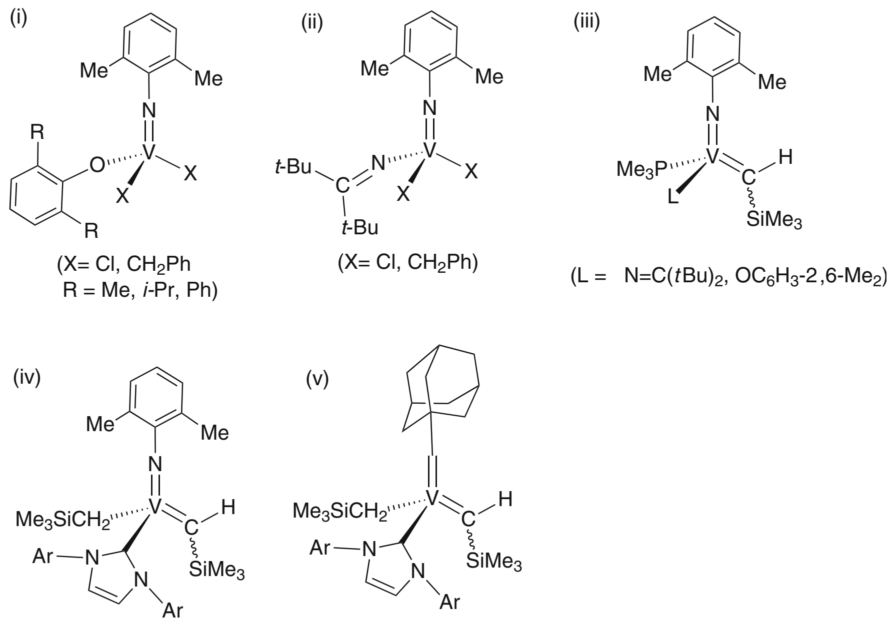


Scheme 7.13 Ring-opening metathesis polymerization via titanacyclobutane

The resulted complex initiates the living ring-opening polymerization of norbornene derivatives without addition of a cocatalyst (Scheme 7.13). The polymer has regulated molecular weights having the titanocyclobutane end group. The rate-determining step resides in the cleavage reaction of the four-membered ring. Addition of aldehyde to the living polymer yields the polymer having the functionalized terminal group due to the addition of the C=O bond to the Ti=C bond [71, 72].

Vanadium (V) complexes which catalyze the ring-opening metathesis polymerization were reported more recently than those using the Mo, W, Ru, and Ti catalysts. Dichlorovanadium complexes with arylimide and bulky aryloxide complexes (Scheme 7.14i, X = Cl) catalyzes ethylene polymerization in the presence of the cocatalyst [73]. The complex having 2,6-di(isopropyl)phenoxy ligand ((i), X = Cl, R = iPr) catalyzes the ring-opening metathesis polymerization of norbornene in the presence of $AlMe_3$ cocatalyst, while the catalyst with Et_2AlCl cocatalyst promotes ethylene polymerization [74].

The dibenzyl complexes ((i) X = CH_2Ph, R = i-Pr) catalyze the ring-opening metathesis polymerization in the absence of a cocatalyst at room temperature. The dichloro complex having a bulky imine ligand ((ii), X = Cl) catalyzes the reaction in the presence of MeMgBr and PMe_3 [75]. Dibenzyl complex ((iii), X = CH_2Ph) is converted to an alkylidene complex ((iv), X = CH_2Ph) upon addition of PMe_3, and the produced complex catalyzes the ring-opening metathesis polymerization of norbornenes [76, 77]. The catalytic activity at room temperature is lower than



Scheme 7.14 Vanadium catalysts for olefin metathesis

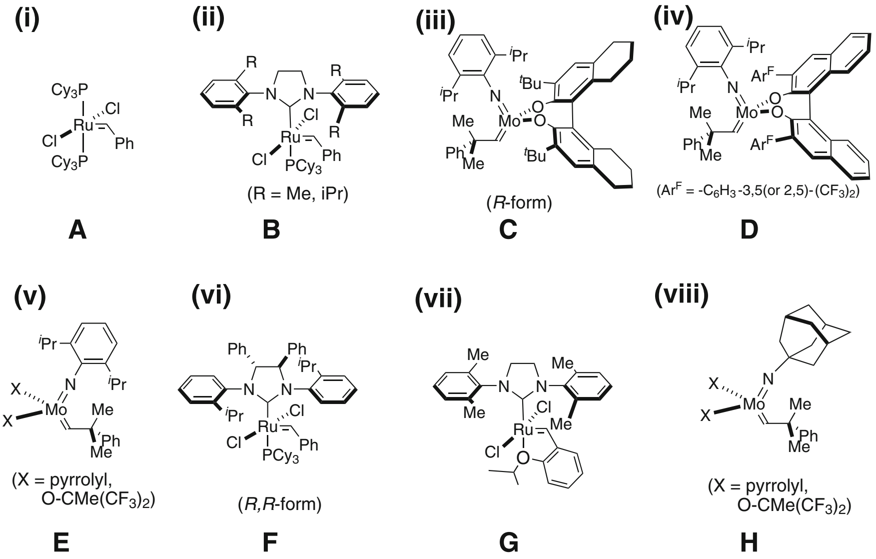
$Mo(CHCMe_2Ph)(N\text{-}(2,6\text{-}i\text{-}Pr)_2C_6H_3)(O\text{-}t\text{-}Bu)_2$, but the vanadium complex shows increased activity even at high temperature (80 °C). Synthesis and properties of the complexes are summarized in a recent review article [78].

7.3 Application of Olefin Metathesis

This section includes development of the olefin metathesis reactions to synthesis of the new target molecules. The Mo and Ru complexes are commonly used as the molecular catalyst. Scheme 7.15 summarizes the catalyst used in this section. Most of the complexes do not require addition of cocatalysts.

7.3.1 Synthesis of the Polymers with New Structures and Functionality

Ring-opening polymerization of norbornene derivatives is utilized to synthesis of the polymer having unique molecular structures and conformations [79]. The monomer equipped with a pyrolidine pendant that is connected to the Zn-porphyrin undergoes polymerization in the presence of Ru catalysts A and B



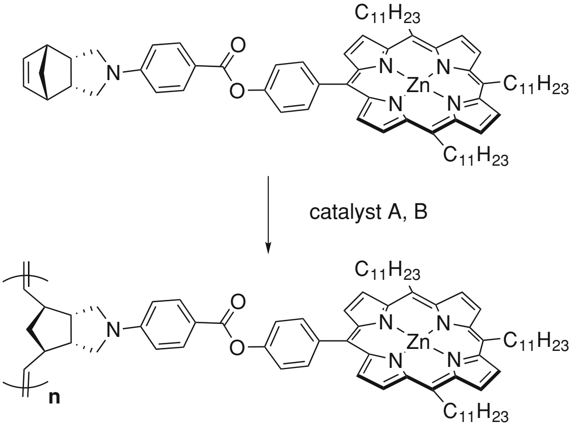
Scheme 7.15 Highly reactive catalysts for olefin metathesis

(Scheme 7.15). The zinc porphyrin groups in the structural units are aligned coherently along the polymer chain [80, 81]. Significant fluorescence quenching is observed, and is attributed to the effective π–π stacking of the porphyrin groups [80] (Scheme 7.16). The monomer with a chiral carbon in the spacer between the porphyrin and norbornene groups is converted to the polymer with a helical conformation [81].

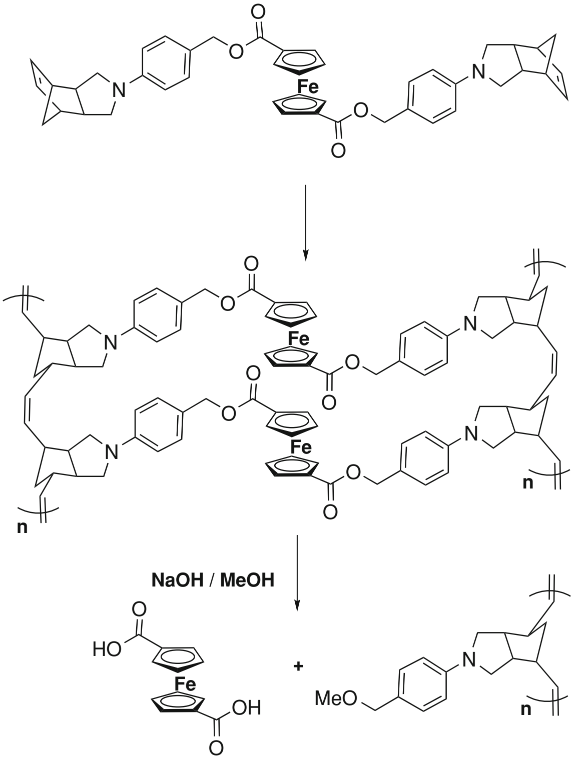
Bifunctional monomer in Scheme 7.17 has two norbornene terminal groups and undergoes the ring-opening polymerization of both groups in a parallel fashion. The obtained polymer has a ladder structure [82–85]. The *cis* isotactic structure of the norbornene polymer as well as the rigid spacer structure between the two norbornene groups of the monomer molecules enabled the efficient formation of the ladder polymer. The aligned ladder structure of the polymer and its helical structure can be observed directly by using STM image techniques.

The strained conformation of the polymer in Scheme 7.17 enhances the interaction of the ferrocenyl groups at close positions. Electrochemical oxidation of the ferrocenylene groups in the polymer to ferrocenium makes the polymer antiferromagnetic owing to the interaction of the neighboring Fe centers. The ladder-type polymer having ester groups between the two polymer strands is converted to the polymer composed of a single chain by hydrolysis of the ester groups. The polynorbornene template formed by the ring-opening polymerization is used in the polycondensation of alkynyl(halo)arene with a similar molecular weights to the starting polymer [86].

Scheme 7.16 Porphyrin-containing poly(norbornene)



Scheme 7.17 Synthesis and degradation of the ladder-type poly(norbornene)



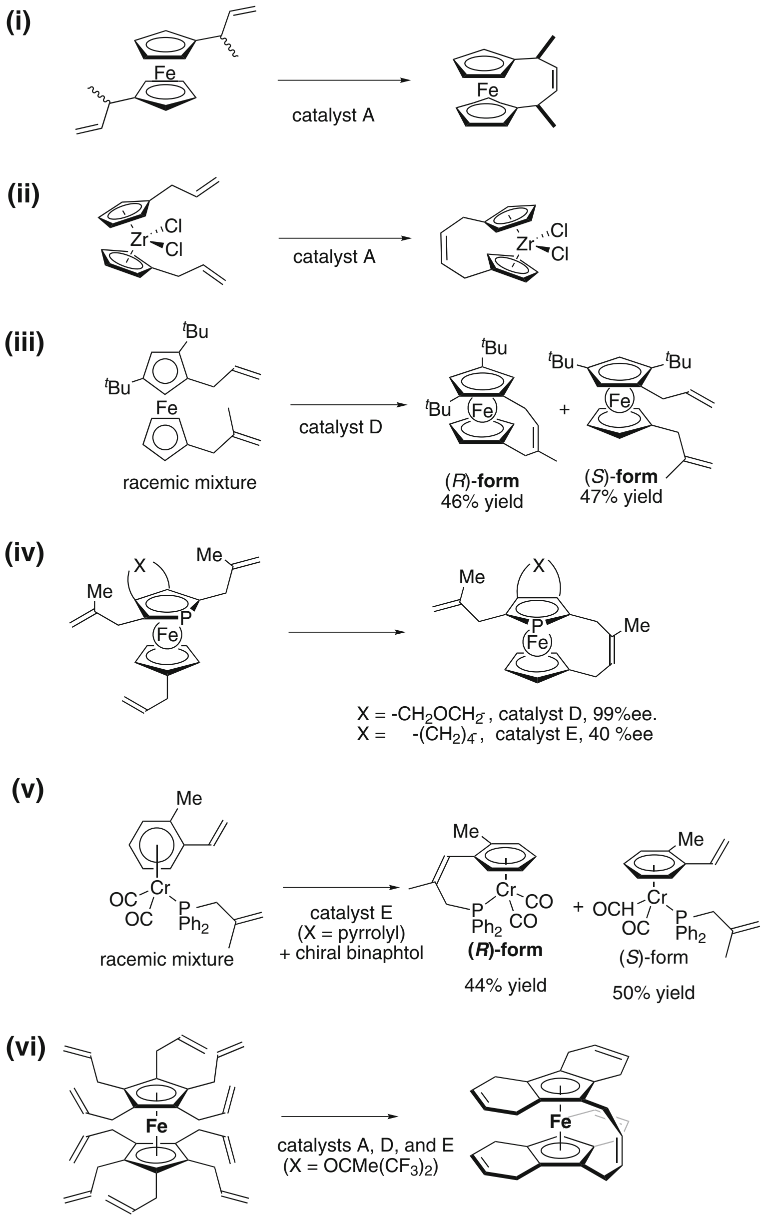
7.3.2 Synthesis and Reactions of the Ligand of Transition Metal Complexes

Most of the transition metal complexes are composed of the metal center which is reactive towards many chemical reagents and the chemically inert ligands. Thus, selective transformation of a ligand of the complexes is not common. Recent successful application of the olefin metathesis reaction to synthesis and modification of the organometallic complexes is mentioned below.

Metallocene derivatives whose two cyclopentadienyl ligands have a vinyl pendant undergo the ring-closing metathesis reaction in the presence of the Ru and Mo catalysts. The ferrocene derivative, and zirconoccene dichloride derivative with the allylic substituents are converted to the metallocenophanes owing to the intramolecular olefin metathesis reactions ((i), (ii) in Scheme 7.18) [87]. Unsymmetrically substituted metallocenes have planar chirality depending on the position of the substituents on the cyclopentadienyl ligands. The ring-closing metathesis of the acyclic metallocene derivatives catalyzed by optically active Mo complexes induces kinetic resolution [88–90]. Ferrocene derivatives having an allyl group and two *tert*-butyl groups on the cyclopentadienyl ligand undergo the ring-closing metathesis reaction in the presence of the Mo catalyst having a chiral binaphtholato ligand (iii).

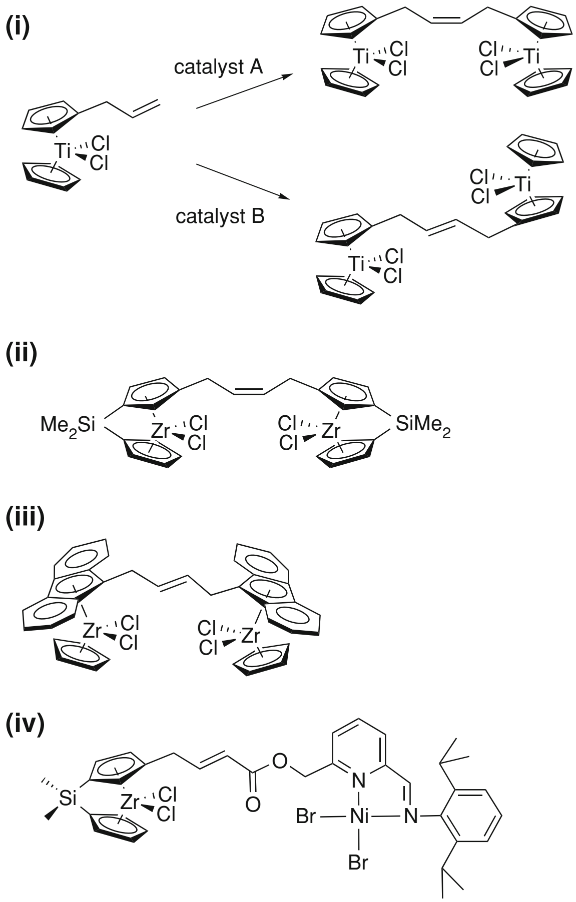
The racemic mixture of the chiral ferrocene derivatives undergo the kinetic resolution during the ring-closing metathesis reaction, which forms the (*R*)-ferrocenophane product and leaves the starting material with (*S*)-configuration. The phosphaferrocene with two equivalent allylic groups in the phosphacyclopentadienyl ligand undergoes the enantiotopos differentiating ring-closing metathesis in the presence of the optically active Mo catalysts and produces one of the chiral ferrocenophanes selectively (iv) [91]. Arene-chromium complex ((v) in Scheme 7.18) also undergoes the ring-closing metathesis with kinetic resolution to form the optically active complex having the arene ligand with the phosphine-containing pendant [92]. The two vinyl groups of a cyclopentadienyl ligand of the ferrocene derivatives produce the ligand with new cyclic groups (vi) [93, 94].

Intermolecular olefin metathesis of the transition metal complexes having the ligand with the terminal alkenyl groups forms the dinuclear complexes having a vinylene linker. Further hydrogenation of the C=C double bond produces the complexes whose metal centers are connected by oligomethylene chains. The dimerization of dichlorotitanocene having the allyl substituent on a cyclopentadienyl ligand affords the dinuclear complex [95]. Use of Ru catalyst A (Scheme 7.15) causes formation of the complex having a *cis*-vinylene group, while the reaction catalyzed by B yields the complex with a *trans* vinylene group (Scheme 7.19i). Dimerization of *ansa*-zirconocene and cyclopentadienyl(fluorenyl)zirconium dichloride [95, 96] was also reported ((ii) and (iii)). These dinuclear complexes are employed as the catalyst for polymerization of ethylene and/or propylene in the presence of MAO catalyst.

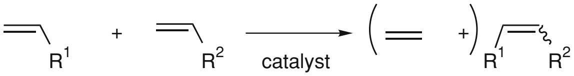


Scheme 7.18 Synthesis of metallocenophanes

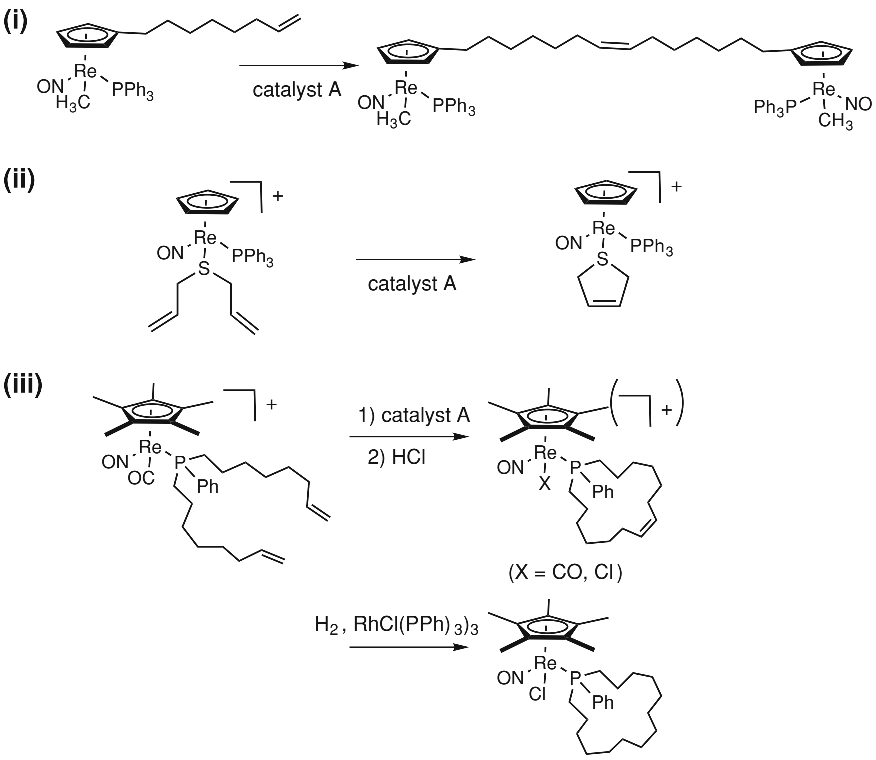
Scheme 7.19 Dinuclear complexes of Ti and Zr



Scheme 7.20 Cross-metathesis reaction



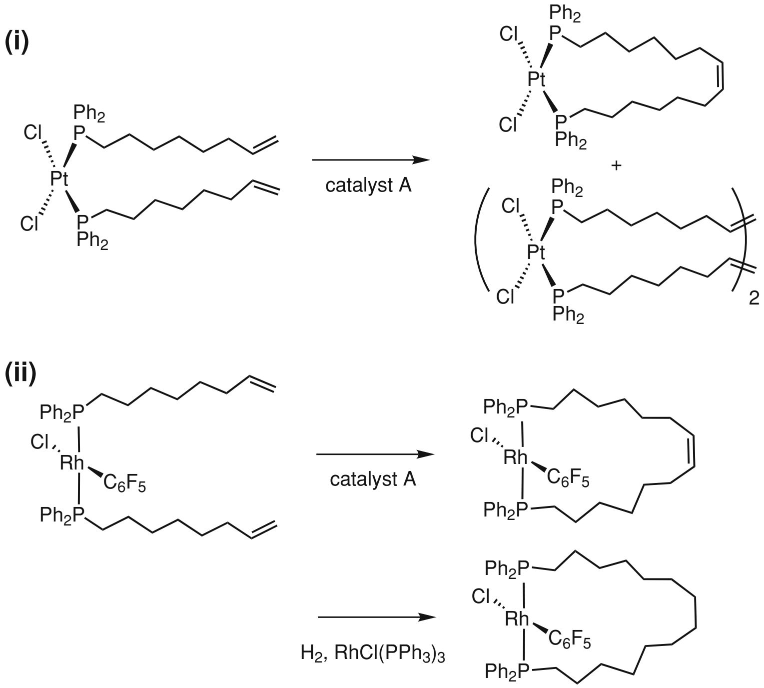
The cross-metathesis reaction, which converts the two terminal olefins into an internal olefin and ethylene, was studied by using the transition metal complexes as the catalyst (Scheme 7.20) [97]. The selective cross-metathesis of α-olefin with acrylic esters was achieved by using the Ru catalyst with an NHC ligand (catalyst B in Scheme 7.15). The reaction is used in the coupling of the two metal complexes having alkenyl pendant groups, and it gave the Zr–Ni complex having vinylene acrylic ester linkage ((iv) in Scheme 7.19) [98]. The complex catalyzes ethylene polymerization to produce the polymer having long (>C10) branches along the polymer chain. The reaction probably involves oligomerization of ethylene on the Ni site and copolymerization of the resulted 1-olefin and ethylene on the Zr center.



Scheme 7.21 Inter- and intra-molecular olefin metathesis of Re complexes

Stable rhenocene complex with 7-octenyl substituent on the cyclopentadienyl ligand undergoes the dimerization in the presence of the Ru catalyst, and produces the dinuclear complexes with a long polymethylene spacer (Scheme 7.21i) [99]. The complex with a ligand having two vinyl groups undergoes the ring-closing metathesis reaction. The *S*– and *P*– ligand with two ω-alkenyl substituents are cyclized *via* the intramolecular ring-closing olefin metathesis reactions. Scheme 7.21ii, iii show the formation of 2,5-dihydrothiophene ligand and the phosphine ligand having a fifteen-membered ring.

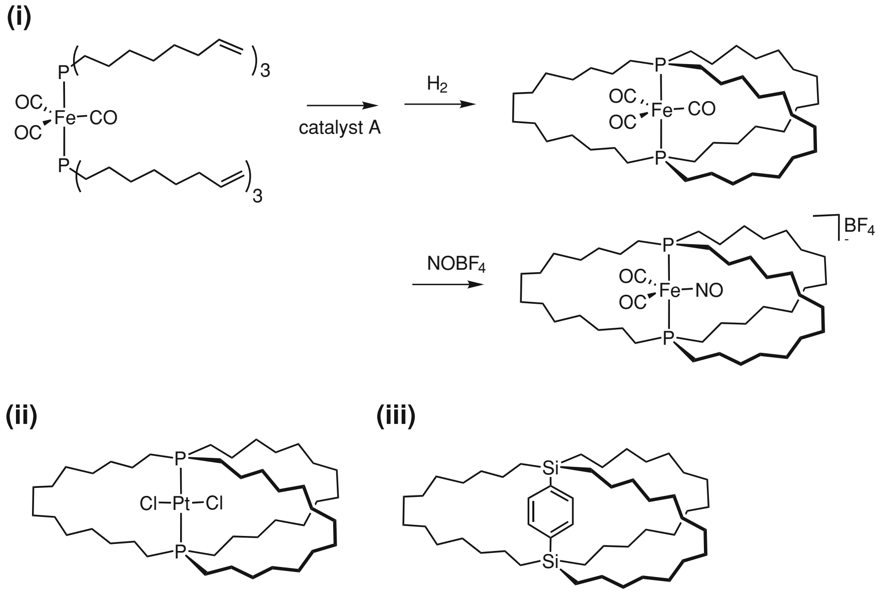
The Pt(II) complexes having two (7-octenyl)diphenylphosphine ligands at the *cis* positions in the square-planar structure are converted to the complex having a diphosphine ligand with a long spacer, but the dinuclear product is also formed by the intermolecular olefin metathesis (Scheme 7.22i) [100]. The ratio of the mononuclear and dinuclear products is 9:91, and they are equilibrated via reversible ring-opening and closing metathesis reactions. The square-planar Rh(I) complex having two alkenyl phosphine ligands at the *trans* positions causes the intramolecular reaction selectively to afford the macrocyclic complex (Scheme 7.22ii).



Scheme 7.22 Olefin metathesis of vinyl groups of the ligand

The Fe(0) complex having two tris(7-octenyl)phosphine ligands at the apical positions of the trigonal bipyramidal structure undergoes triple intramolecular olefin metathesis of the vinyl groups to form the complex having three polymethylene spacers between the two phosphorus atoms ((i) in Scheme 7.23) [101]. X-ray crystallographic results demonstrated that the three CO ligands and three oligomethylene chain are orientated to a staggered directions. Oxidation of the complex with $NOBF_4$ produced the cationic complex with an NO ligand. The Pt analogue was also reported, and the complex is demetalated by KCN to leave the multicyclic bisphosphine (ii) [102].

1,4-Bissilylphenylene derivative having three 7-octenyl substituents on an Si atom is converted to the tricyclic compound with three oligomethylene spacers between the two Si atoms (iii) [103]. The central phenylene plane is rotated on the ^{2}H NMR time scale even in the crystalline state within the cage made of the three oligomethylene chains. The crystalline phase transition occurs around 310 K, which is attributed to change of the velocity of the rotation of the phenylene group. Accompanying change of the birefringence of the crystals is observed [104, 105].



Scheme 7.23 Molecular gyroscope

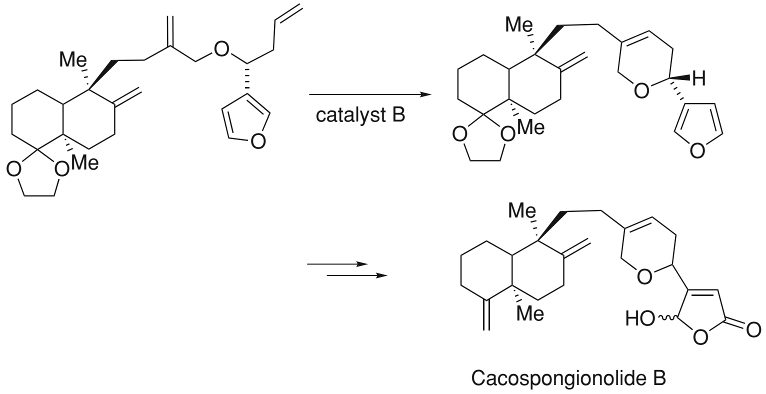
7.3.3 Synthesis of Natural Products

Many natural products contain a macrocylic ring system in the molecule, and its chemical synthesis requires efficient ring-forming reactions. The reaction should be chemo-, regio-, and stereo-selective and should be conducted under the conditions which are not disturbed by the functional groups of the materials and products.

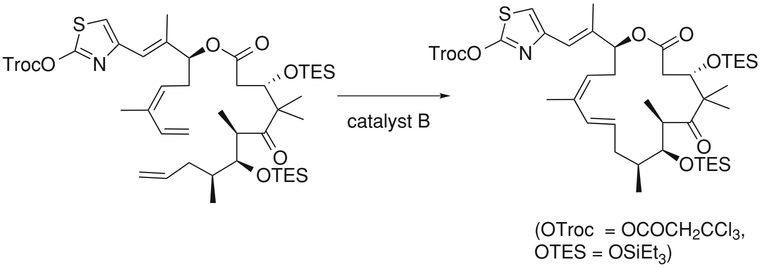
Ring-closing metathesis reaction was used in the total synthesis of marine sponge metabolites, cacospongionolide B (Scheme 7.24) [106]. The intermediate having a 2-alkyl-4-(3-furyl)-3-oxa-1,7-octadiene group undergoes the ring-closing metathesis to form a new six-membered ring in the presence of the Ru catalyst at room temperature. The product is obtained in high yield (81 %) and selectivity, and is further converted to the target compound after four additional reaction steps.

The total synthesis of epothilone 490 achieved by Danishefsky involved the ring-closing metathesis reaction to form a macrocycle (Scheme 7.25) [107]. The product is obtained in 40 %, and derived to the target compound by removal of the protecting groups. The other possible product with a smaller ring size due to the metathesis of the internal olefin was not formed in the model reactions.

The ring-closing metathesis reaction was also employed in the total synthesis of spongidepsin (Scheme 7.26) [108]. The reaction using the Ru catalyst at 110 °C produced the macrocyclic product in 80 %. Hydrogenation of the resulted vinylene



Scheme 7.24 Synthesis of Cacospongionolide B

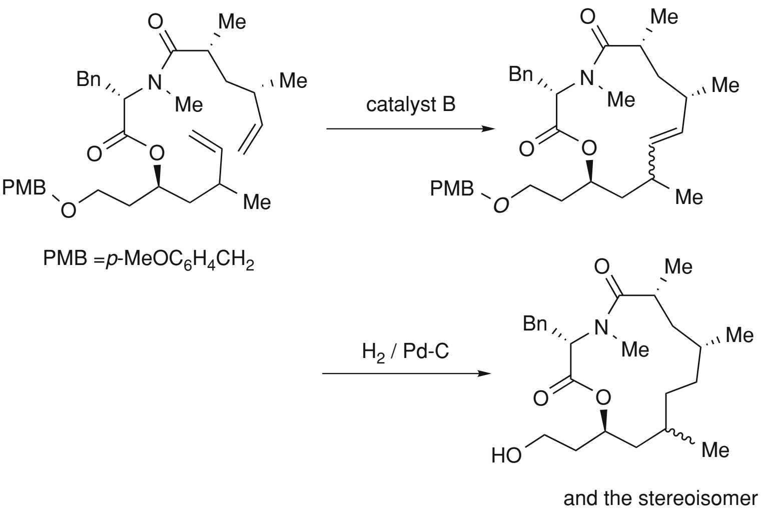


Scheme 7.25 Synthesis of Epothilone 490

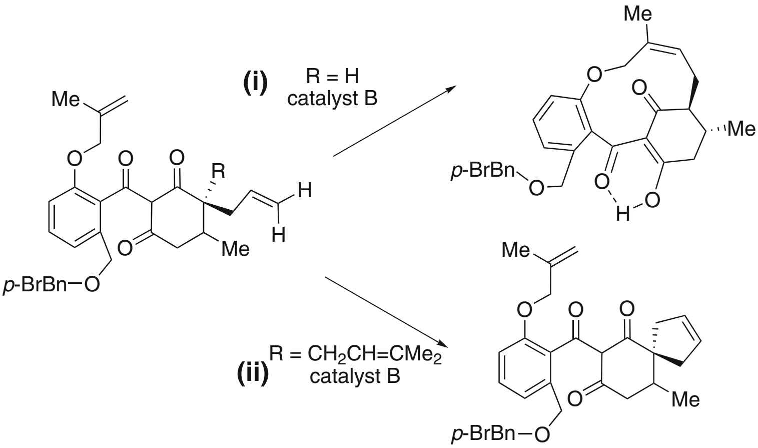
group afforded the saturated macrocycle, and one stereoisomer of the products has the same stereochemistry as that of the natural compound.

Coleophomones A-D are the functionalized cyclic molecules, and each of them is of interest from the view of pharmacological activity. Nicolaou used the ring-closing metathesis reaction in their total synthesis study [109]. The intermediate with an allyl group at the α-position of the cyclic 1,3-dione (R=H in Scheme 7.27) is converted to the cyclized product having a 11-membered ring (i). The yield is 30 % in spite of the complicated dynamic stereochemistry of the molecule. (*E*)-Vinylene stereochemistry of the product agrees with the natural product. The starting material remained after the reaction (35 %) was recovered from the reaction mixture. The substrate with two allyl groups at the same carbon forms the compound with a five-membered ring in 85 % yield after 1 h (ii).

Total synthesis of ciguatoxin CTX3C was achieved by Hirama in 2001 [110–113]. He employed the ring-closing olefin metathesis reaction at almost the final step to form the central nine-membered ring from the diene precursor. The first-generation Grubbs catalyst promoted selective ring-closing reaction at 40 °C without ring-opening of the already existing cyclic olefin groups (Scheme 7.28).



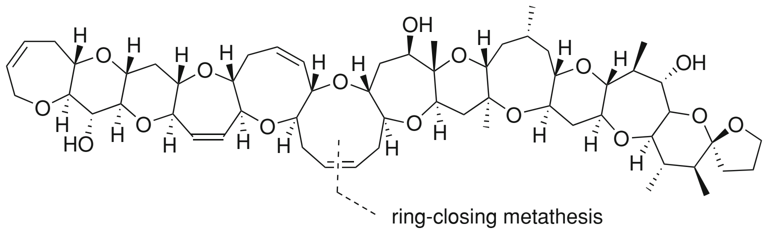
Scheme 7.26 Synthesis of Spongidepsin



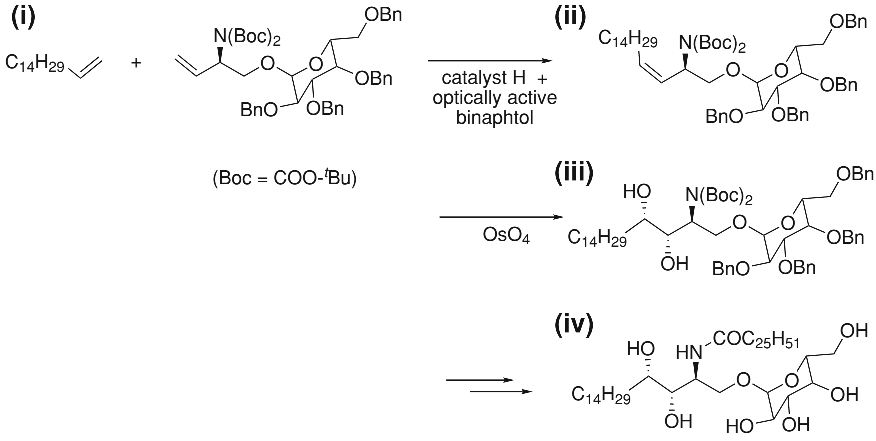
Scheme 7.27 Synthesis of Coleophomones

The yield of the cyclization, in conjunction with the two preceding reaction steps, attained to 60 %, and deprotection of the product afforded the target molecule.

Cross-metathesis reaction is also used in the synthesis of natural organic compounds. The Mo catalyst with a binaphtolate ligand, designed by Schrock, was found to catalyze the cross-metathesis of two 1-olefins to afford the compounds with a *cis*-vinylene group. The reaction was applied to synthesis of potent immunostimulant KRN7000 (Scheme 7.29) [114]. Cross-metathesis of 1-olefin with the protected allylamine with a sugar substituent (i) yields the product having



Scheme 7.28 Ciguatoxin CTX3C



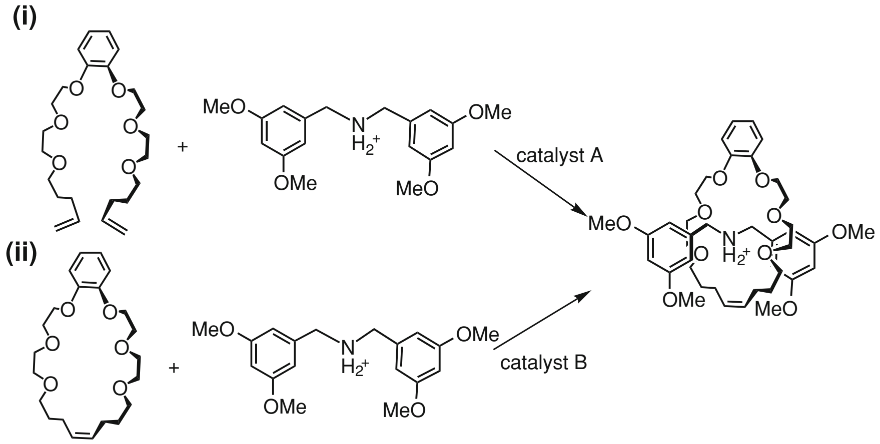
Scheme 7.29 Synthesis of KRN7000

a *cis*-vinylene group (ii). *cis*-Dihydroxylation using OsO_4 forms compound (iii) which is converted to KRN7000 (iv).

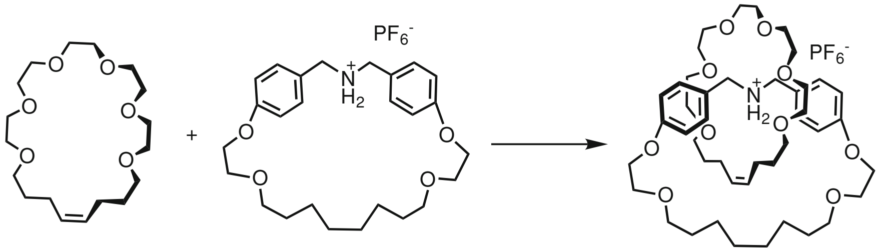
Ring-closing metathesis and olefin metathesis reactions are used in synthesis of many other natural products [115–118].

7.3.4 Interlocked Molecules

Interlocked molecules such as catenane (ring and ring) and rotaxane (axle and ring) are expected to behave in a different way from a single molecular compound in the solution, and attract recent research attention. Ring-closing olefin metathesis reaction to yield a large cyclic compound is employed to their formation. Attractive intermolecular interaction between the molecules such as multiple hydrogen bonds and strong π–π interaction etc. stabilizes the intermediate for the formation of the interlocked molecules by enthalpy factors. The reversible nature of the olefin metathesis often enhances the formation of the interlocked molecular



Scheme 7.30 Clipping synthesis of rotaxane

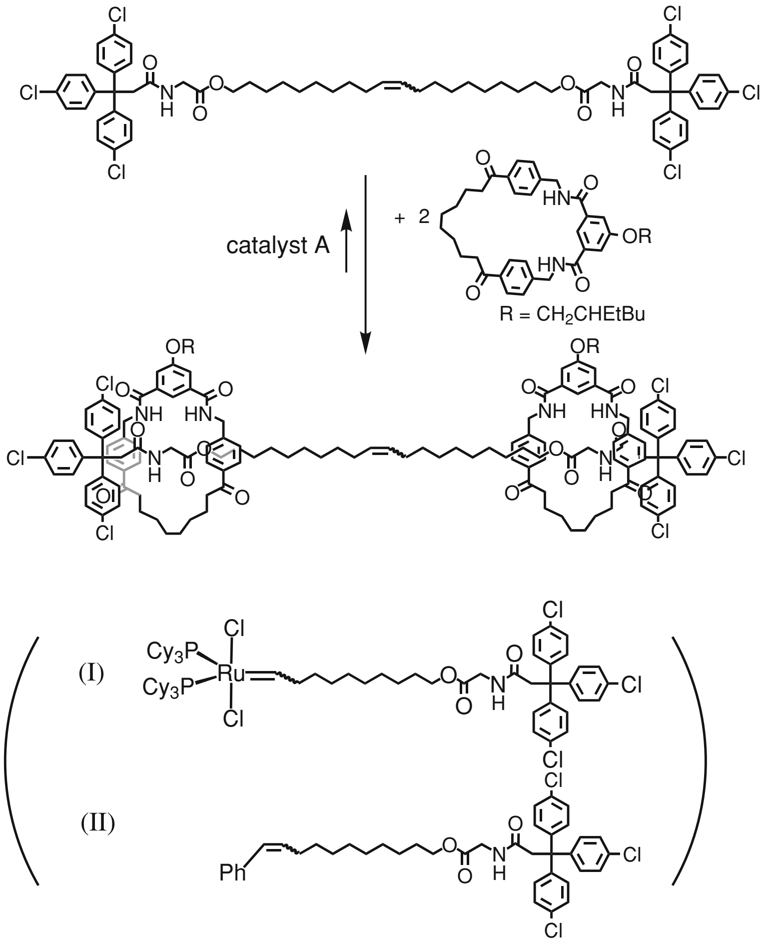


Scheme 7.31 Synthesis of catenane

systems. Ring closing metathesis reaction of the polyethylene oxide derivative having two terminal vinyl groups in the presence of bis{(3,5-dimethoxy)phenylmethyl}ammonium forms the rotaxane which is stabilized by the O–H···N hydrogen bonding (Scheme 7.30i) [119]. Once-formed rotaxane does not cause detachment of the cyclic and acyclic components owing to too small cavity size of the cyclic component to allow slippage of the bulky 3,5-dimethoxyphenyl group.

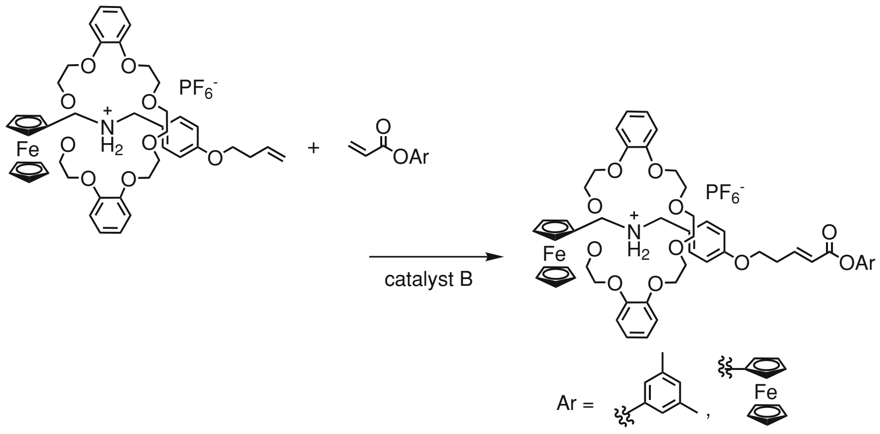
Reaction of the crown ether having a C=C bond with bis(benzyl)ammonium forms [2]rotaxane in the presence of catalyst B (Scheme 7.30ii). Repetition of opening of the cyclic compound and its reclosing yields the rotaxane which is stabilized by hydrogen bonding between the ammonium group and oligoethylene oxide groups.

Such macrocycle formation is utilized also to the synthesis of catenane containing the macrocyclic polyethylene oxide having a vinylene group and the macrocyclic dialkylammonium (Scheme 7.31) [120]. Formation of a similar crown ether and its use as the component of pseudo-rotaxane was also reported [121].



Scheme 7.32 Synthesis of [3]rotaxane via Ru-alkylidene intermediate

The other strategy for synthesis of the rotaxane is to apply the reversible olefin metathesis reaction to the axle molecule that has a C=C double bond [122]. The molecule is composed of the bulky terminal groups, and functional groups to accommodate the macrocyclic compound and the vinylene group at the center of the oligoethylene chain which binds the terminal groups (Scheme 7.32). Addition of the Ru catalyst to a mixture of the axle and macrocyclic component molecules forms the two fragments of the axle, I and II, which are in equilibrium with the axle molecule by reversible olefin metathesis reactions. The –CH=CH-Ph terminal group of II is able to pass through the cavity of the macrocyclic molecule, and forms a pseudorotaxane. The olefin metathesis of the pseudorotaxane with the fragment I or self-metathesis of II results in the formation of [1]- and [2]-rotaxanes, respectively.

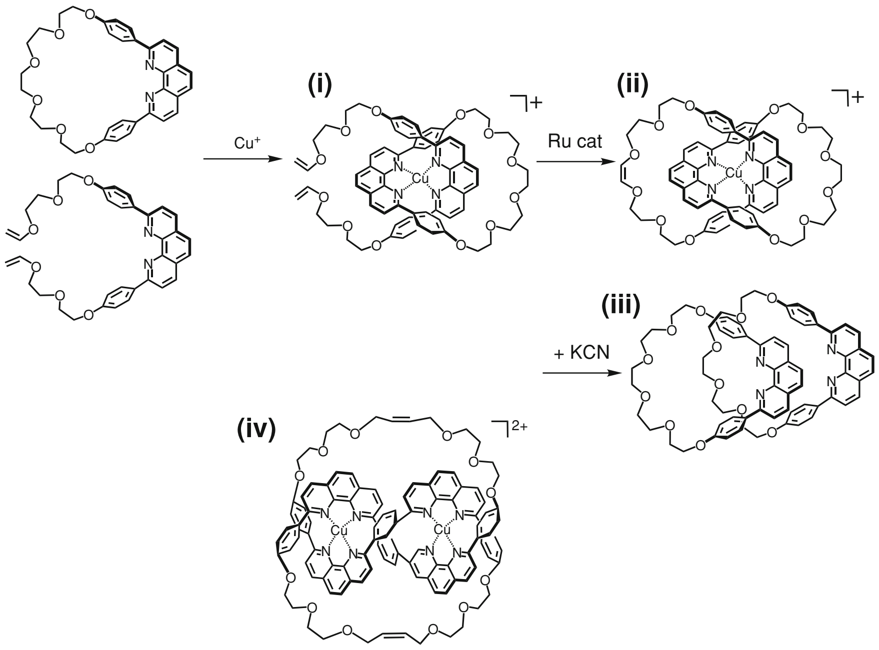


Scheme 7.33 End-capping synthesis of rotaxane

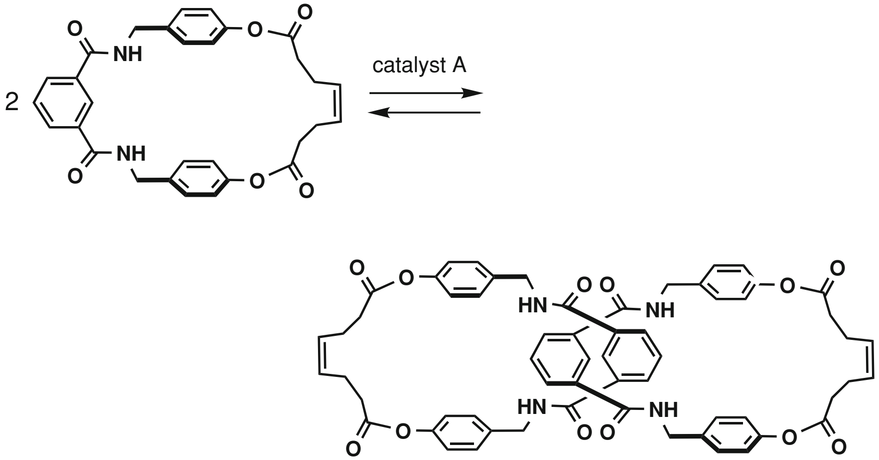
Synthesis of the rotaxane using this strategy becomes useful by using the cross-metathesis reactions which binds the two different fragments selectively. Cross-metathesis of terminal alkene with acrylic ester is promoted by the Ru catalyst [96], and the reaction of the pseudorotaxane having an alkenyl terminal group with the bulky acrylic ester forms the rotaxane in high selectivity (Scheme 7.33) [123–128].

Combination of the ring-closing metathesis with the metal template aggregation of the molecules provides an efficient oligoethylene oxide method for the catenane formation (Scheme 7.34) [129, 130]. The macrocycle oligoethylene oxide having 1,10-phenanthroline group and the acyclic compound having the same functional groups and terminal vinyl groups form the tetrahedral Cu(I) complex ((i) in Scheme 7.34). The intramolecular ring-closing metathesis reaction of the two vinyl groups results in the interlocked molecule with the coordination of the Cu(I) center to the two phenanthroline ligand (ii). Further addition of CN^- to the solution causes removal of the metal center from the molecular system. The resultant organic part is composed of two macrocyclic molecules interlocked with each other (iii). This strategy is applied to the molecular system which contains the helical stereochemistry within the catenane, a molecular knot [131]. The compound (iv) in Scheme 7.34 is converted to the organic molecular knot by hydrogenation of the vinylene groups and demetalation.

Preparation of catenane from the two macrocyclic molecules having a vinylene group was also reported [132]. Addition of the Ru catalyst to the solution of the macrocyclic compound in Scheme 7.35 causes formation of the catenane made of the two molecules. The motivation for formation of the entropically unfavorable catenane is in the multiple hydrogen bonds between the functional groups of the cyclic molecules. An amide group of the macrocyclic molecule accepts two O–H···N hydrogen bonds from the amide groups of the other molecule and two N–H···O hydrogen bonds from the ester groups. The equilibrium is shifted to

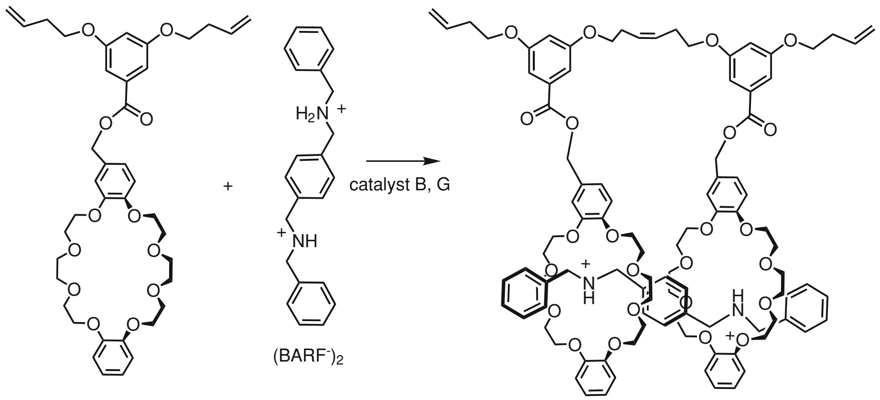


Scheme 7.34 Template synthesis of rotaxane and molecular knots

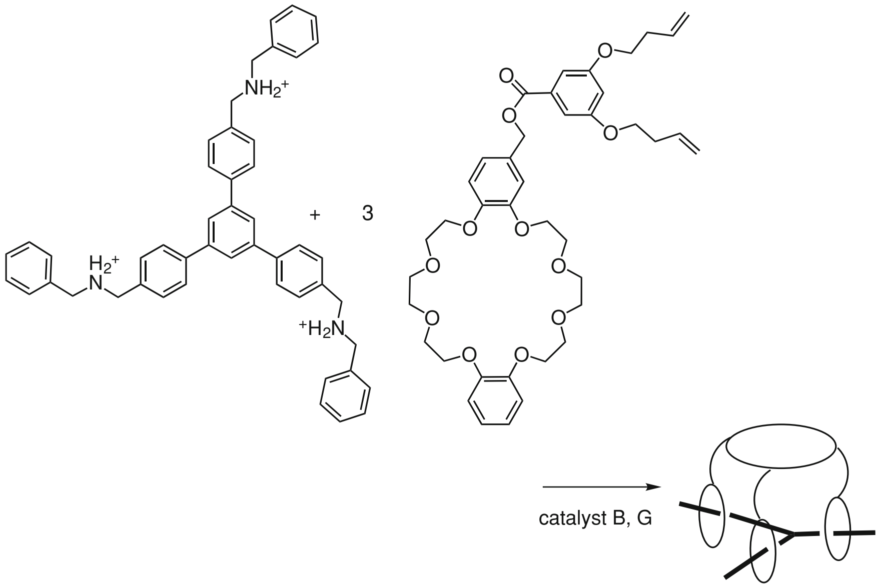


Scheme 7.35 Synthesis of catenane from macrocycles

formation of the catenane in a concentrated solution (>95 % in 0.2 M) and to dissociation in a diluted solution (<5 % in 0.0002 M).



Scheme 7.36 Dimerization of diene using a rotaxane template



Scheme 7.37 Cyclotrimerization of diene using a rotaxane template

Selective dimer formation of the acyclic diene using the rotaxane template was reported (Scheme 7.36) [133]. The molecules having an aromatic core equipped with two vinyl group-containing substituents and a crown-ether group at 1,3,5-positions form the dimer selectively by intermolecular metathesis reaction of one of the vinyl groups of each molecule.

Formation of [3] pseudorotaxane template enhances the dimer formation efficiently.

Addition of a three-armed aromatic compound to three equivalent crown ether molecule having an aromatic pendant with two alkenyl groups in the presence of the Ru catalyst caused cyclotrimerization of the latter molecules via intermolecular olefin metathesis with the aid of the template formation (Scheme 7.37) [134]. Yield of the trimer attains to 55 % when catalyst G is employed.

The dialkylammonium molecule equipped with the oligoethylene oxide acts as the precursor of the daisy-chain type supramolecules [135].

7.4 Conclusion

The olefin metathesis reactions started as the unknown chemical processes, and during the half century, has become indispensable means for synthesis of the polymers, organic and inorganic molecules, and complicated aggregated molecules. It enabled a number of synthetic organic reactions which had been difficult to be achieved. The highly active transition metal catalysts have already reported, and their revision are still continuing. Further progress of this field may enable the novel olefin metathesis catalysis which will change the molecules having olefin groups under the particular kinds of reaction conditions such as in the organs of the living objects.

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Chapter 8
Cross-Coupling Polymerization

Take-aki Koizumi and Takaki Kanbara

Abstract Organometallic cross-coupling reactions directed toward the synthesis of aromatic polymers are reviewed. The progress of this methodology has made the syntheses of numerous functional polymers possible, which includes the synthesis of well-defined π-conjugated polymers and buildup molecular architectures. The polycondensation has been spread out to material areas ranging from optical and electronic materials to biological sensing materials. The use of organometallic direct arylation and carbon-heteroatom bond formation for the synthesis of functional polymers has also been dealt with.

8.1 Introduction

The organometallic catalyzed cross-coupling reactions of various organometallic (Mg, Zn, Sn, B, and Si) reagents and aryl halides to form new carbon–carbon bonds have emerged as versatile synthetic techniques that are widely employed for the syntheses of a variety of organic compounds [1–9]. The pioneering work of Profs. Heck, Suzuki, and Negishi on the Pd-catalyzed cross-coupling reactions in organic synthesis was recognized with the 2010 Nobel Prize in Chemistry [10–12]. Recently a wide range of aromatic functional materials has been developed using such cross-coupling reactions.

The most commonly employed transition metal catalysts in cross-coupling reactions are nickel and palladium-based complexes. The general mechanism of the reactions is shown in Scheme 8.1 [1–9]. In general, cross-coupling reactions involve

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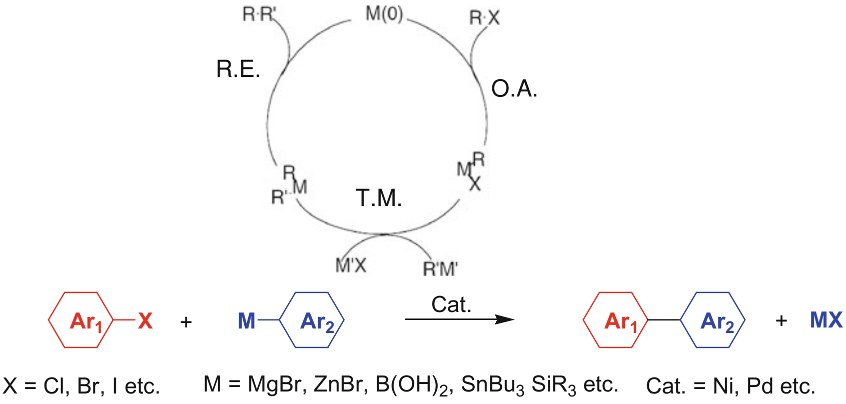
Lecture Notes in Chemistry 85, DOI: 10.1007/978-3-662-43539-7_8,



Scheme 8.1 Transition metal catalyzed cross-coupling reaction

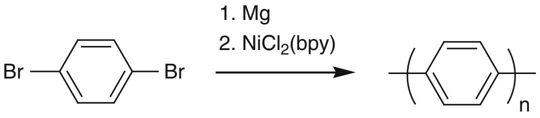
three steps: an oxidative addition reaction across the C-halogen bond as an electrophile, transmetalation with the main group in the organometallic reagents acting as nucleophiles, and reductive elimination resulting in the formation of the carbon-carbon bond and regeneration of the active catalyst. Organometallic reagents such as Grignard reagents (Kumada-Tamao-Corriu) [1m], zinc (Negishi) [1n], stannane (Migita-Kosugi-Stille) [1o], boron (Suzuki-Miyaura) [1p], silane (Hiyama) [1q], copper (Sonogashira) reagents [1r], or lithium and mercury compounds can be used.

In the field of polymer chemistry, cross-coupling reactions are particularly important in the synthesis of conjugated aromatic oligomers and polymers [13–17]. Over the last three decades, conjugated polymers have attracted widespread attention owing to their high conductivity and interesting optoelectronic properties, resulting in their application to optoelectronic devices such as light emitting diodes, field-effect transistors, and photovoltaic systems. Organometallic methodologies are useful for preparing well-defined conjugated polymers, especially when a high regioselectivity is required in the polymeric backbone [18, 19]. Since the development of conducting polymers by Profs. Heeger, MacDiarmid, and Shirakawa in 1977, which was recognized with the 2000 Nobel Prize in Chemistry [20–22], various aromatic monomers have been employed to develop conjugated polymers. This chapter describes the organometallic catalyzed cross-coupling polycondensation used in the synthesis of various conjugated polymers. The utilization of organometallic carbon-heteroatom bond formations in the synthesis of functional polymers is also described.

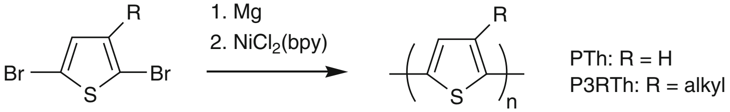
8.2 Ni-Catalyzed Polycondensation

The application of transition metal catalyzed cross-coupling reactions to polymeric materials was first reported by Yamamoto and co-workers in the synthesis of poly(*p*-phenylene), which is prepared by nickel-catalyzed Grignard coupling of

1,4-dibromobenzene [23–25]; one of the C–Br bonds reacts with magnesium to form the Grignard reagent, which undergoes further coupling reaction (Eq. 8.1). Polythiophene (PTh) and poly(3-alkylthiophene)s (P3RThs) were prepared using the same protocol (Eq. 8.2) [26]. The introduction of the alkyl group to PTh resulted in enhanced solubility of the polymer. The nickel-catalyzed polycondensation of dihalogenated-thiophenes in the presence of zinc also yielded PTh derivatives (Eq. 8.3) [27].



(8.1)



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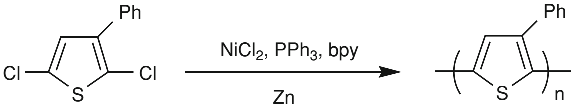


(8.3)

The reactions are simple and they yield several conjugated aromatic polymers with well-defined linkages between the monomer units. However, the regioregularity cannot be controlled using this protocol (Chart 8.1). The synthesis of regioregular poly(3-alkylthiophene)s (P3RThs), which involve head-to-tail (HT) repeating units, such as poly(3-hexylthiophene) (HT-P3HTh), can be realized by the Ni-catalyzed polycondensation of regio-controlled organomagnesium reagents. This is achieved by the regioselective lithiation of 2-bromo-3-alkylthiophene with lithium diisopropylamide (LDA), followed by transmetalation with magnesium bromide, yielding an organometallic intermediate (Chart 8.2a) [28]. Regio-controlled organozinc reagents also afforded regioregular P3RThs (Chart 8.2b) [29]. Regioregular poly(3-hexylthiophene) (HT-P3HTh) is of particular interest because the polymer exhibits remarkable physical properties such as higher crystallinity and electrical conductivity in the solid state, as compared to the regio-random polymers [13, 30, 31]. Their application to flexible electronic devices such as organic thin-film solar cells and organic field effect transistors has been investigated.

Because the molecular weight of the polymer prepared by condensation polymerization is generally difficult to control, the polydispersity index theoretically approaches two at high conversions. Both Yokozawa and McCullough groups reported the first chain-growth synthesis of regioregular P3RThs via the

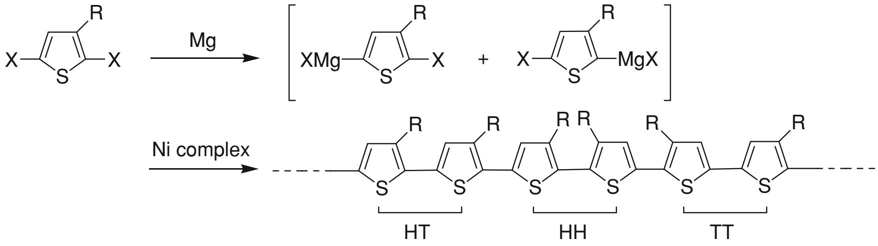


Chart 8.1 Synthesis of regioirregular poly(3-alkylthiophene)

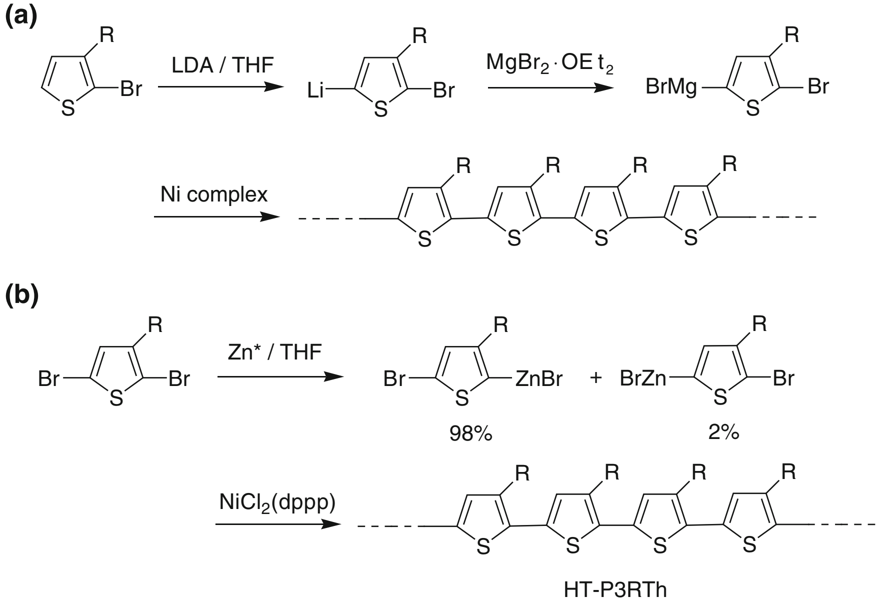
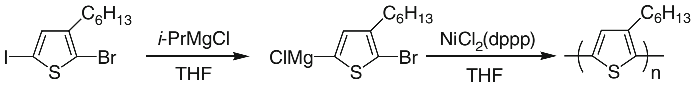


Chart 8.2 Synthesis of regioregular poly(3-alkylthiophene)

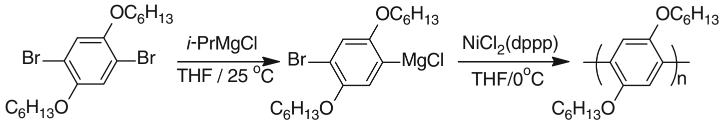
polymerization of Grignard-type monomers catalyzed by dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) ($NiCl_2$(dppp)) (Eq. 8.4). The products have controlled molecular weights and narrow molecular weight distributions (M_w/M_n ratios around 1.1, M_n up to 28,700 g/mol) [18, 19, 32, 33]. The M_n values and the M_w/M_n ratios of the polymers were strongly affected by the ligands of the Ni catalyst (dppp > dppe > PPh_3; dppe = 1,2-bis(diphenylphosphino)ethane). In these reactions, the regio-controlled Grignard reagent was prepared by a selective Grignard exchange reaction with *i*-PrMgCl. The C–H functionalization of 2-chlorothiophene derivatives with the formation of magnesium amides in situ also afforded similar regio-controlled Grignard monomers [34, 35].



(8.4)

In their proposed mechanism, the chain-growth polymerization is induced by the “ring-walking process” of the Ni catalyst, whereby the Ni(0) species is transferred intramolecularly along a polymer chain to its end, where it oxidatively inserts into the C–Br bond (Chart 8.3) [36].

Owing to the protocol, all polymer chains are equipped with the same end groups, i.e., bromine and hydrogen atoms after quenching with acid. Therefore, it can allow control of the molar mass by adjusting the feed ratio of the monomer to the Ni catalyst. The catalyst-transfer condensation polymerization has also been demonstrated for other monomers; well-defined conjugated polymers such as polyphenylenes, polypyrroles, and polyfluorenes have been prepared (Eqs. 8.5–8.7) [18, 19, 37–39].



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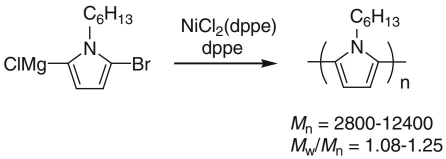

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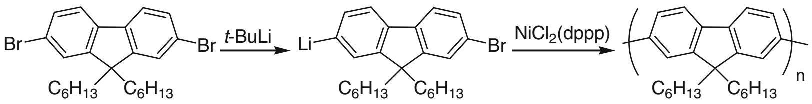


(8.7)

The important advantage of this catalyst-transfer condensation polymerization over other methods is the possible formation of block copolymers by successive monomer additions (Chart 8.4) [40]. Because several aromatic monomers undergo catalyst-transfer condensation polymerization in a living polymerization manner, a variety of block copolymers has been synthesized by successive polymerizations performed in one pot (Chart 8.5) [18, 19, 38, 41–44].

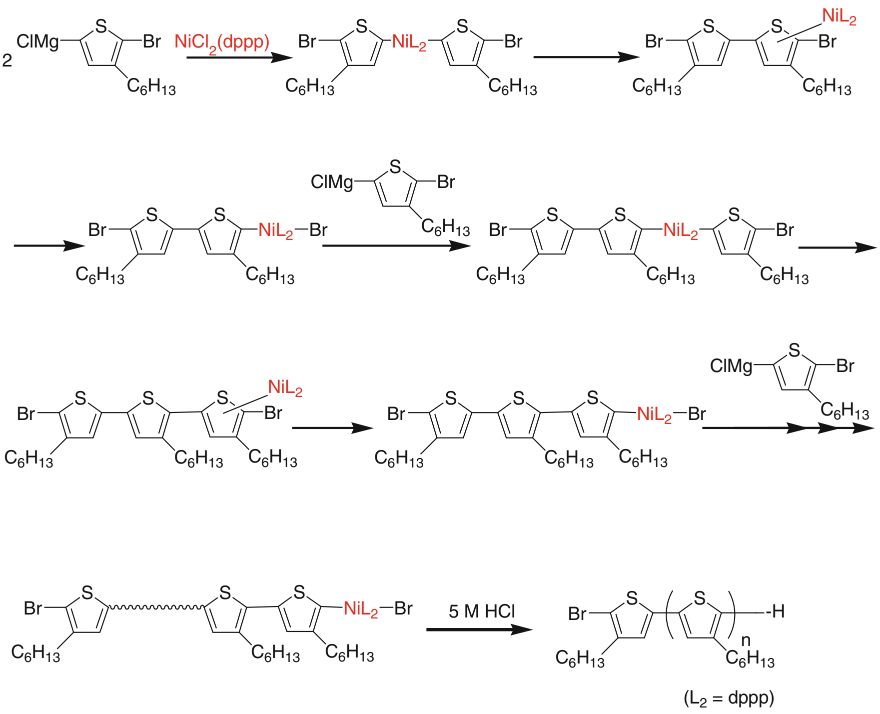


Chart 8.3 Chain-growth synthesis of poly(3-hexylthiophene)

8.3 Pd-Catalyzed Polycondensation

During the early development of cross-coupling reactions, Ni complexes were identified as useful reagents and catalysts. In the intervening years, more attention was invested in the development of Pd catalysts, particularly for Pd-catalyzed Migita-Kosugi-Stille, Suzuki-Miyaura, Sonogashira, and Mizoroki-Heck coupling reactions. These reactions have been utilized in the synthesis of a variety of conjugated polymers owing to some inherent advantages such as increased diversity and tenability of the catalysts, oxidative and aqueous stability, and relatively facile isolation and structural analysis of the complexes, which aids their mechanistic and methodological developments [13–17].

The Migita-Kosugi-Stille coupling reaction is a versatile carbon-carbon bond formation between stannanes and aryl halides (Eq. 8.8), whereas the Suzuki-Miyaura coupling reaction is the palladium-catalyzed cross-coupling reaction between organoboronic acid and aryl halides (Eq. 8.9) [1–12, 17]. One important difference between the Suzuki-Miyaura and the Migita-Kosugi-Stille coupling reactions is that in the former reaction, the boronic acid requires activation, for example with a base. This activation of the boron atom enhances the polarization

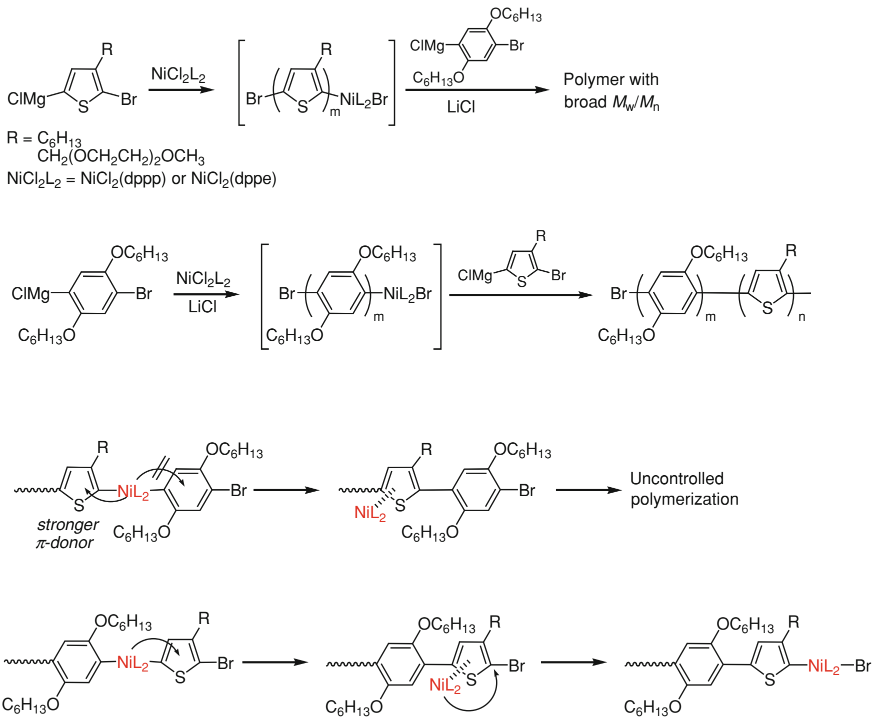
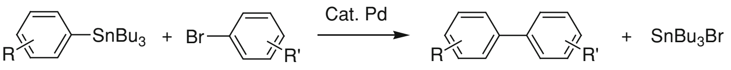


Chart 8.4 Synthesis of block copolymer by the catalyst-transfer condensation polymerization

of the organic substituent, and facilitates transmetalation, as shown in Scheme 8.2. Recently developed catalysts and methods have broadened their possible applications enormously, so that the range of the reactants is not restricted to aryls, but also includes alkyls, alkenyls, and alkynyls.



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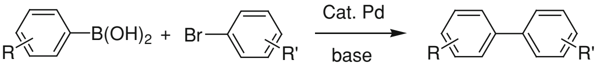
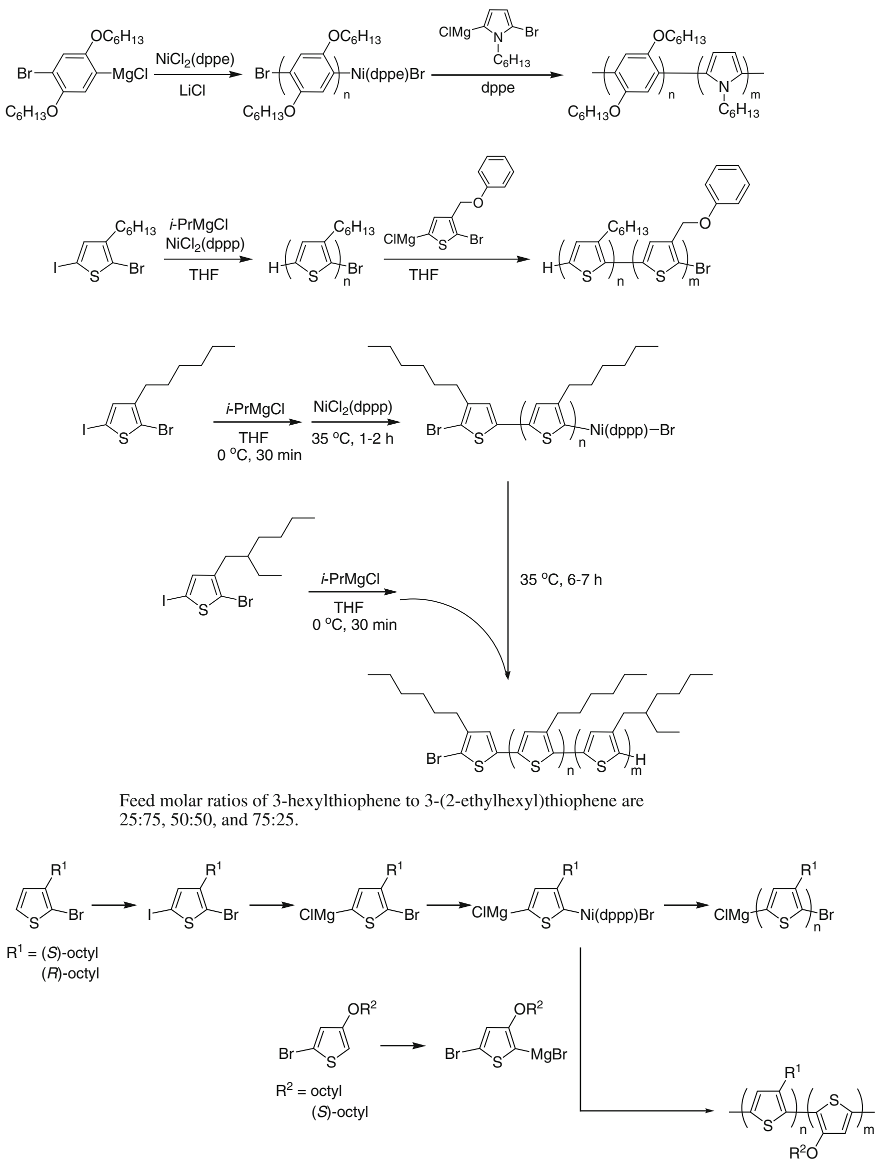


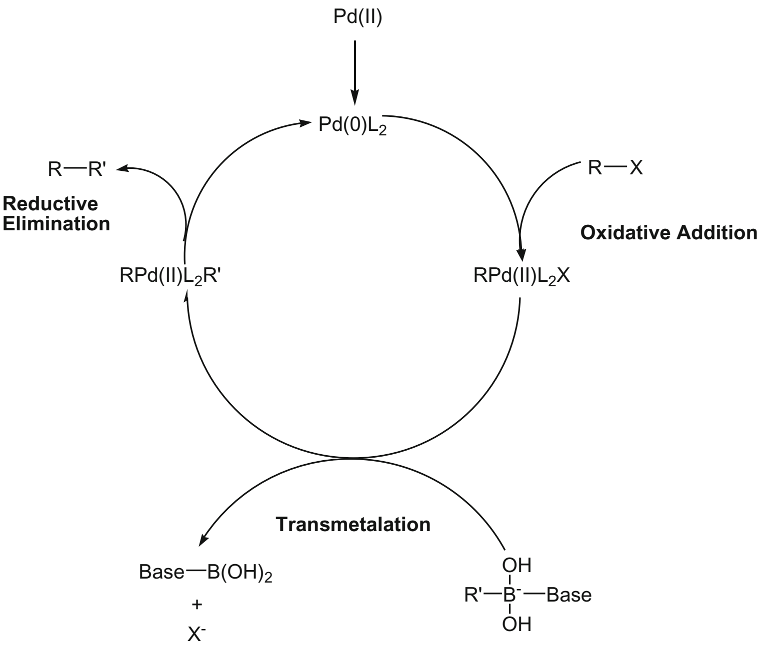
(8.9)

The major advantage of these cross-coupling reactions is that they can tolerate various functional groups and proceed under mild reaction conditions. The Suzuki-Miyaura coupling reaction can be conducted even in aqueous media. Because the aryl halides involved can be extensively functionalized before subjecting them to



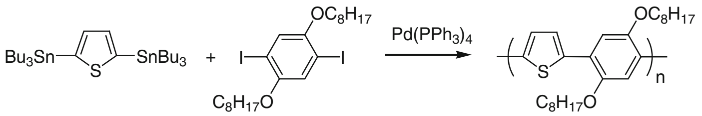
Feed molar ratios of 3-hexylthiophene to 3-(2-ethylhexyl)thiophene are 25:75, 50:50, and 75:25.

Chart 8.5 Synthesis of several block copolymers in one pot

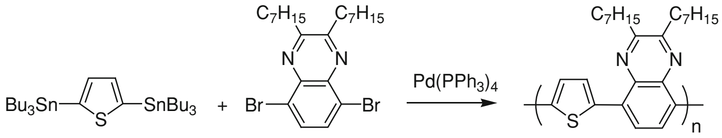


Scheme 8.2 Suzuki-Miyaura coupling reaction

the coupling reaction, these reactions allow for the preparation of different products from all of the combinations of halides and stannanes or boron reagents. This feature of the coupling reactions offers the opportunity to design a variety of conjugated polymers as well as alternating copolymers with functional moieties manifesting many highly desirable properties (Eqs. 8.10–8.12) [16, 17, 45–47].



(8.10)



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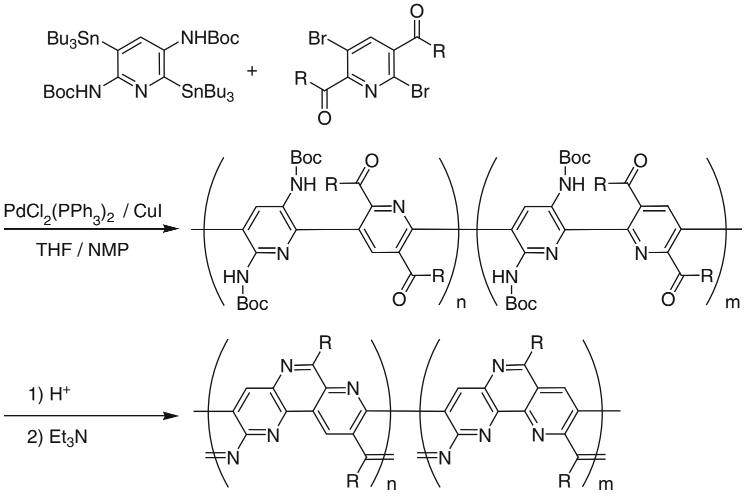
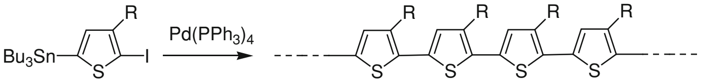
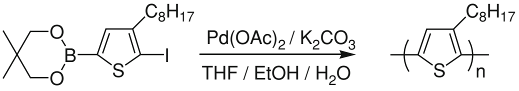


(8.12)

The coupling reactions can also yield highly regioregular poly(3-alkylthiophene)s (HT-P3RTh), when the 3-alkylthiophene derivatives shown in Eqs. 8.13 and 8.14 are employed [48, 49].

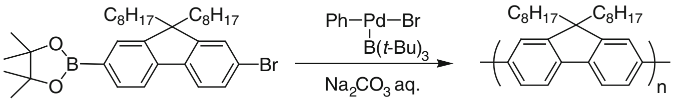


(8.13)

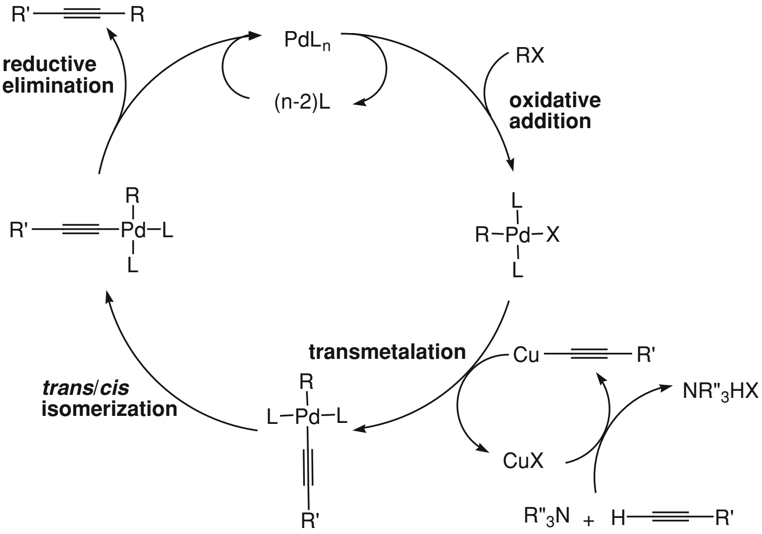


(8.14)

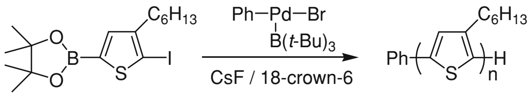
Catalyst-transfer condensation type Suzuki-Miyaura coupling polymerization was achieved by Yokozawa and coworkers (Eqs. 8.15 and 8.16) [50, 51]; polyfluorene with a narrow polydispersity has also been prepared. The polycondensation proceeded in a chain-growth polymerization manner from the initiator unit derived from the Pd catalyst.



(8.15)

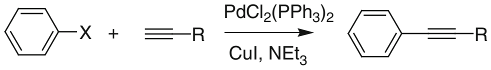


Scheme 8.3 Sonogashira coupling reaction



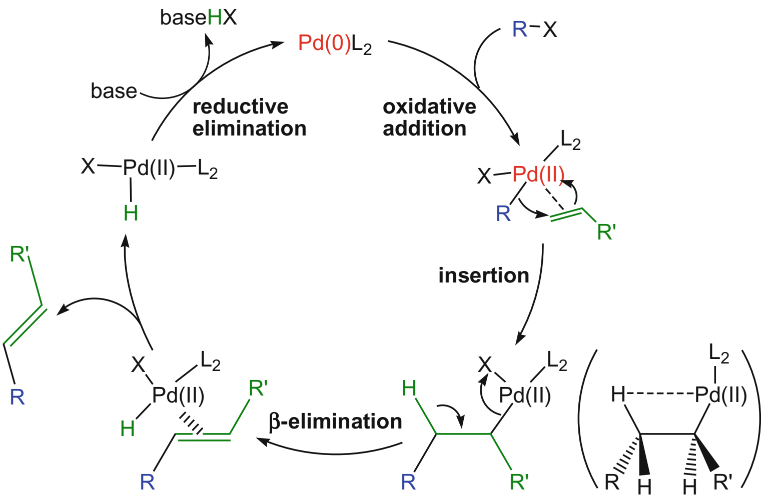
(8.16)

The Pd-catalyzed cross-coupling reaction of aryl and vinyl halides with terminal alkynes employing co-catalytic copper(I) halides and an amine base is known as the Sonogashira coupling reaction (Eq. 8.17) [1–9]. In this reaction, copper(I) halides react with the terminal alkyne and produce copper(I) acetylide, which acts as an activated species for the coupling reactions. Then, transmetalation proceeds in the usual manner for the Pd complex (Scheme 8.3). Because the reaction forms C_{sp}–C_{sp2} bonds, the polycondensation between dihalogenated and diethynyl aromatic compounds gives poly(arylene ethynylene) type conjugated polymers (Chart 8.6) [14, 52].



(8.17)

The Mizoroki-Heck reaction is the palladium-catalyzed addition of aryl, vinyl, or substituted vinyl groups to aryl halides or triflates (Eq. 8.18) [1–9, 12]. The Mizoroki-Heck reaction differs significantly from the other Pd-catalyzed cross-coupling reactions because (1) it involves an insertion step after the oxidative addition step, and (2) the coupling products are produced via a β-hydrogen



Scheme 8.4 Mizoroki-Heck coupling reaction

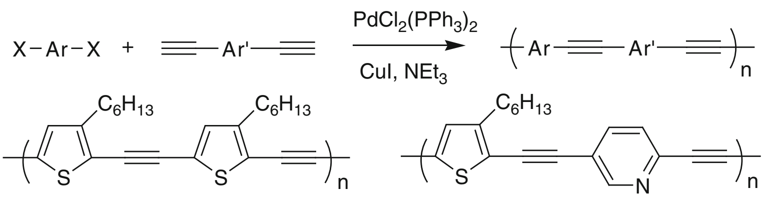
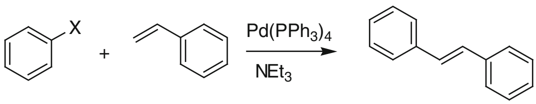


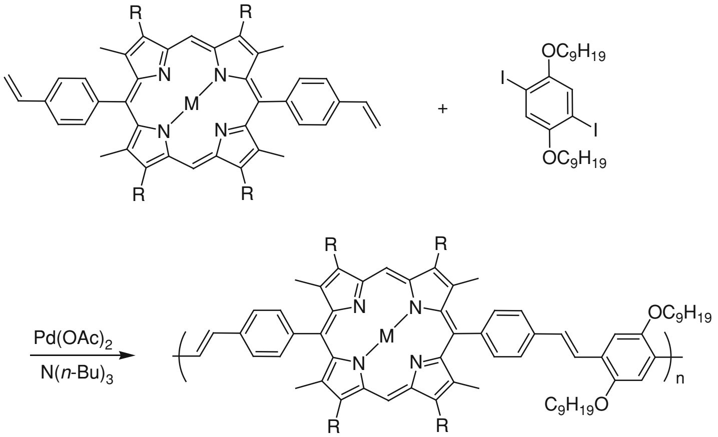
Chart 8.6 Synthesis of poly(arylene ethynylene)s

elimination, whereas the other coupling products are associated with reductive elimination (Scheme 8.4).

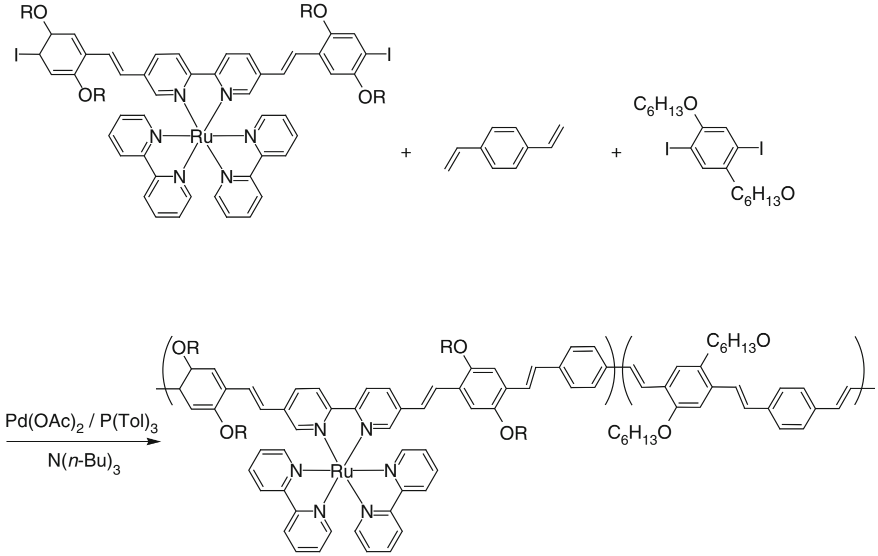


(8.18)

In the β-hydrogen elimination step, the atom in the Pd–C–C–H group must be included in a plane for the reaction to take place, as this is a *syn* elimination process. For steric reasons, the R group will tend to eclipse the smallest group on the adjacent carbon as elimination occurs, leading predominantly to a *trans* double bond in the product. Owing to this *trans* selectivity, the Mizoroki-Heck reaction has been successfully applied to the synthesis of several poly(phenylene vinylene) (PPV) analogs having *trans*-C=C bonds. PPV analogs have attracted considerable attention owing to their high electrical conductivity and optoelectronic properties harnessed in electroluminescent applications (Eqs. 8.19 and 8.20) [53, 54].



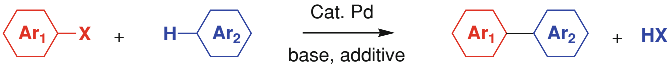
(8.19)



(8.20)

Recently, the catalytic dehydrohalogenative cross-coupling of heteroarenes with aryl halides (a so-called direct arylation) has attracted a great deal of attention as an alternative to the various cross-coupling reactions described above (Eq. 8.21)

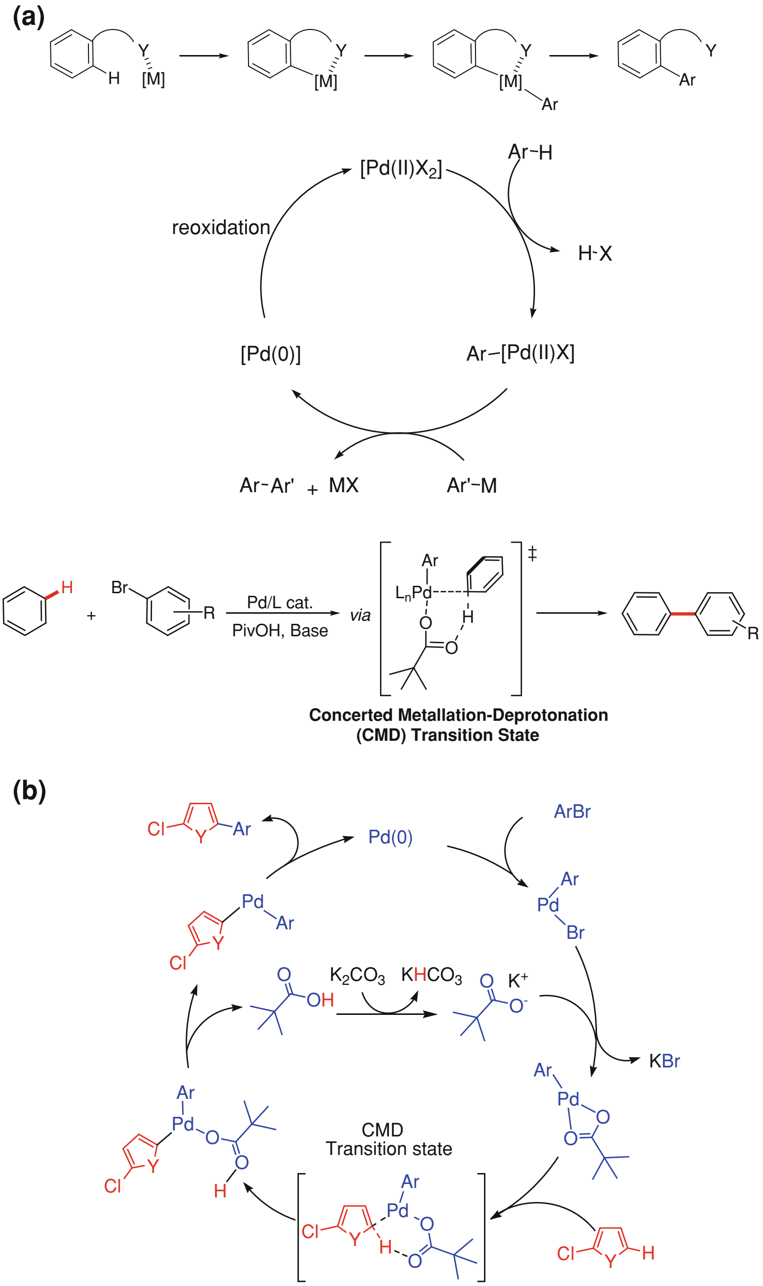
[55, 56]. Since this class of cross-coupling reactions does not require preparation of organometallic reagents and does not form metallic salts as a by-product, this method serves as a cost-effective and environmentally friendly alternative for the preparation of arylated heteroaromatic compounds.



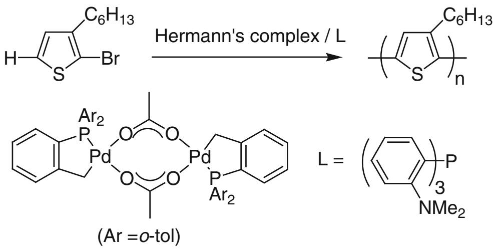
(8.21)

The most common mechanism of C–H bond cleavage promoted by a metal is electrophilic aromatic substitution (SE_{Ar}) involving the reaction of an electrophilic metal catalyst with an electron-rich, nucleophilic aromatic ring. Cyclometalation-based approaches constitute the general strategy towards the arylation of C–H bonds, which results in the functionalization of the *ortho* position to a directing group (Scheme 8.5a). Alternatively, a mechanism based on the metal/base-promoted cleavage of C–H bonds involving a concerted metalation-deprotonation (CMD) pathway has been proposed, instead of the SE_{Ar}. In this mechanism, the carboxylato ligands act as an internal base to achieve the deprotonation of the arenes and the concurrent metalation (Scheme 8.5b). It has been found that palladium(II) acetate is generally the best source of the transition metal catalyst to be used, because the acetate ligand is believed to play multiple roles in cyclometalation reactions. In terms of the iron-catalyzed direct arylation, the transformation proceeds through an aryl radical transfer pathway [57]. The development and mechanistic studies of C–H functionalization are currently underway.

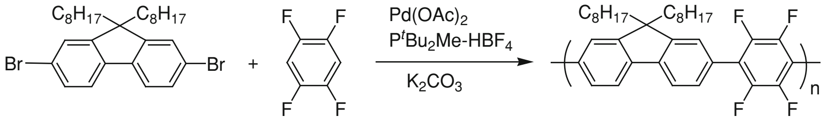
The direct arylation protocol should be of great benefit to polymer synthesis with respect to reducing the waste formation and decreasing number of the reaction steps. However, the development of dehydrohalogenative polycondensation reactions can prove a significant challenge owing to the highly efficient regioselective cross-coupling bond formation required to achieve well-defined linkages between the monomer units. Ozawa and co-workers successfully synthesized poly(3-alkylthiophene)s with high molecular weight and high regioregularity via direct arylation of 2-bromo-3-hexylthiophene ($M_n = 30{,}600$ g/mol, $M_w/M_n = 1.60$). The key to the high catalytic performance reported is the use of Hermann's complex (*trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium) and tris(*o*-*N*,*N*-dimethylaminophenyl)phosphine as catalyst precursors (Eq. 8.22) [58]. The dehydrohalogenative polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene yields the corresponding conjugated polymer with a high molecular weight ($M_n = 31{,}500$ g/mol) (Eq. 8.23) [59]. This is attributed to the fluorine substituted aryl compounds which causes the effective direct arylation leading to the coupling products in excellent yields [60].



Scheme 8.5 Catalytic direct arylation with **a** organometallic reagents and **b** aryl halides

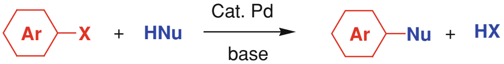


(8.22)



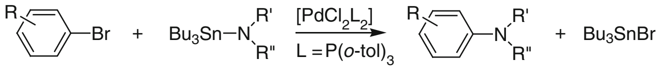
(8.23)

As described above, Pd-catalyzed cross-coupling reactions have proven to be a powerful method for the formation of carbon–carbon bonds, and they are extensively employed across a wide range of areas in synthetic organic chemistry. Meanwhile, the transition-metal catalyzed carbon-heteroatom bond forming reactions have rapidly become valuable synthetic tools because aryl amines and aryl esters are ubiquitous in numerous fields of chemistry (Eq. 8.24) [3, 61–66]. In terms of polymer chemistry, the Pd-catalyzed synthesis of aryl amines by the reaction of aryl halides with primary or secondary amines, commonly known as the Buchwald-Hartwig cross-coupling reaction, has particularly attracted much attention because triarylamine-based polymers are reported to be suitable for use in organic optoelectronic devices, as well as being investigated as typical high-spin organic materials.

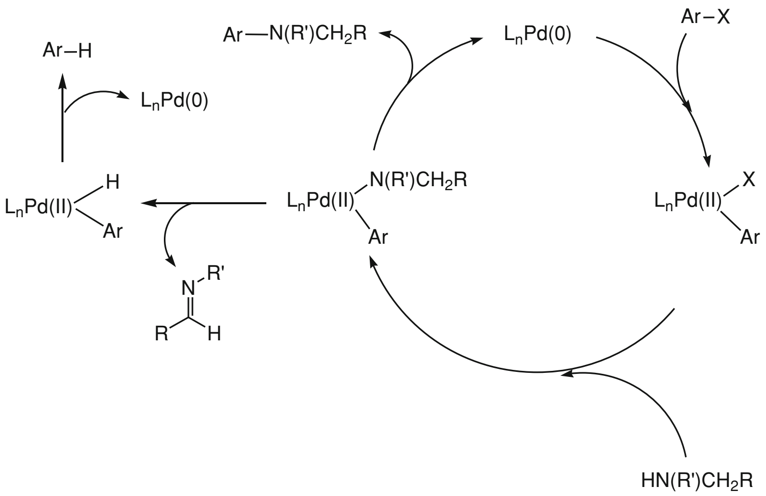


(8.24)

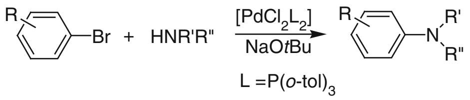
The first Pd-catalyzed aryl amination reaction, reported by Migita and coworkers, is shown in Eq. 8.25 [67]. The reaction was considered to proceed in the same way as the Migita-Kosugi-Stille coupling reaction via the transmetalation of the tin amide compounds to the Pd complex. Problems associated with the use of stannane reagents were overcome by the Buchwald and Hartwig groups (Eq. 8.26) through the use of sodium *tert*-butoxide as a base [68, 69]. This base was effective in the deprotonation of the reacting amine, and the sodium amide generated in situ was used instead of the corresponding tin amide species.



(8.25)



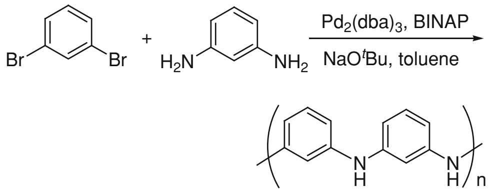
Scheme 8.6 Buchwald-Hartwig cross-coupling reaction



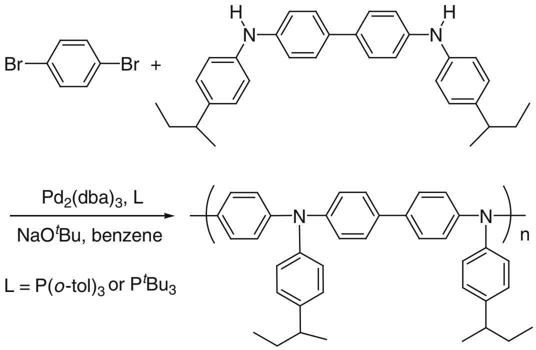
(8.26)

The generally proposed mechanism for this transformation is shown in Scheme 8.6. The catalytic cycle is believed to involve the oxidative addition of an aryl halide, followed by the coordination and deprotonation of the amine. Finally, the reductive elimination of the *N*-aryl product takes place. Since the side products form via β-hydrogen elimination, design of the catalyst systems, especially selection of the ligand, plays a key role in the aryl amination reaction.

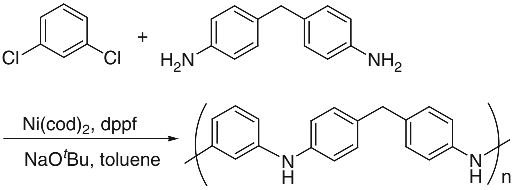
The Buchwald-Hartwig cross-coupling reaction is an efficient tool for syntheses of poly(*m*-aniline) analogs and poly(triarylamine)s, which are rarely prepared by conventional oxidative polymerization. Because the ligand in a catalytic system plays an important role in smooth polymerization, it is essential to choose a suitable ligand for the desired polymer structure. 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is a suitable ligand for the synthesis of poly(*m*-aniline) analogs bearing a secondary amine unit (Eq. 8.27). Tri-*t*-butylphosphine (P^tBu_3) is one of the optimal ligands for the synthesis of poly(triarylamine)s (Eq. 8.28) [70–74]. Analogous Ni-catalyzed aryl amination reactions have also been applied to polycondensation (Eq. 8.29) [75].



(8.27)

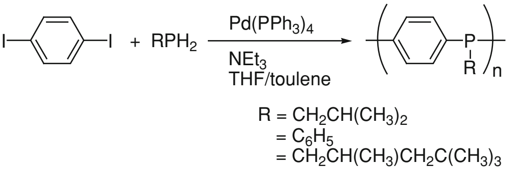


(8.28)



(8.29)

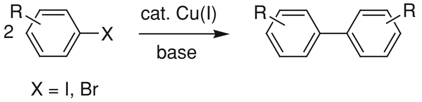
Other Pd-catalyzed carbon-heteroatom (i.e., C–O, C–S, C–P) bond forming reactions essentially proceed in the same manner. The polycondensation using a C–P coupling reaction yields poly(*p*-phenylphosphine) (Eq. 8.30); analogs of polyaniline exhibit electronic delocalization through the extension of conjugation through the phosphorus atom [76–78].



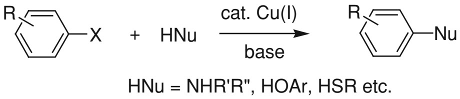
(8.30)

8.4 Cu-Catalyzed Polycondensation

Since copper is a cheaper metal with lower-toxicity than Pd and Ni, an increased interest in the Cu-catalyzed cross-coupling reaction, referred to as the Ullmann condensation, has arisen. This is supported by the recent observations that appropriate ligands can modulate the reactivity of less reactive transition metals than Pd etc. and achieve effective and versatile catalytic systems [79–82]. The classical Ullmann reaction is defined as the synthesis of symmetric biaryls using Cu-catalyzed coupling (Eq. 8.31). Meanwhile, "Ullmann-type" cross-coupling reactions include Cu-catalyzed nucleophilic aromatic substitutions between various nucleophiles (e.g., substituted phenoxides) with aryl halides (Eq. 8.32).



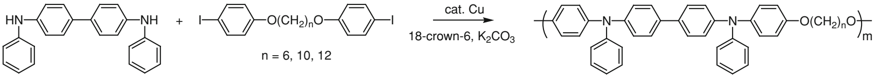
(8.31)



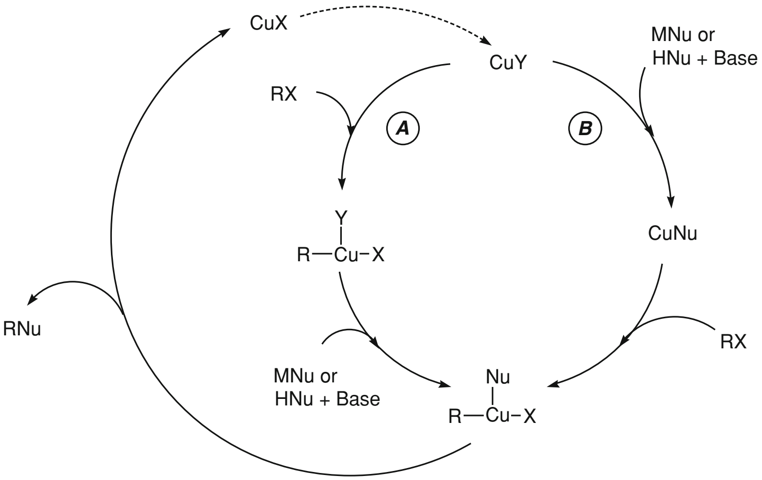
(8.32)

Copper can take part in the cross-coupling chemistry in a way similar to palladium as shown in Scheme 8.7. The most important difference with respect to copper is an easy accessibility of four oxidation states (0 to +3) of the metal; the cross-coupling catalytic cycle with copper is most likely served by the +1/+3 oxidation states.

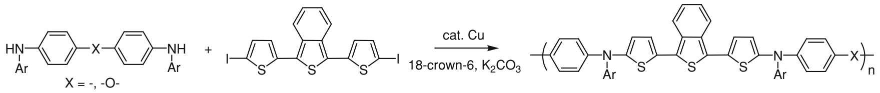
The classical Ullmann coupling reaction has several drawbacks including the necessity of high reaction temperatures and of large amounts of copper. However, with the development for milder reaction conditions and increasing tolerance to sensitive functionalities, the deficiencies of the conventional Ullmann coupling reactions have been overcome. The modified Ullmann coupling reaction in the presence of 18-crown-6 as a phase transfer catalyst was adopted for the synthesis of soluble poly(triarylamine)s (Eq. 8.33) [83]. The coupling reaction procedure could also be used to prepare poly(triarylamine)s containing light-harvesting dyes with a low band gap (E_g < 1.8 eV) (Eq. 8.34) [84]. The combination of CuCl/ quinoline and sodium hydroxide is a suitable catalyst/ligand and base system for preparation of hyperbranced poly(phenylene oxide) (Eq. 8.35) [85]. Analogous Cu-catalyzed aryl amidation of aromatic dihalides with diamides yielded the corresponding aromatic polyamides (Eq. 8.36) [86, 87].



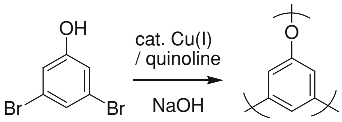
(8.33)



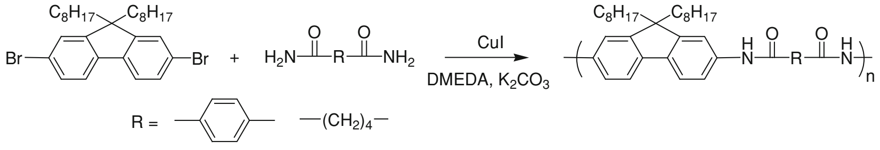
Scheme 8.7 Ullmann-type cross-coupling reaction



(8.34)



(8.35)



(8.36)

8.5 Recent Topics of the Polymers Synthesized by Using Cross-Coupling Polymerization Methods

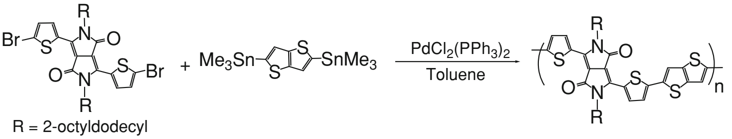
The development of diverse cross-coupling methods has made possible the preparation of a wide variety of polymers containing various monomer units. As mentioned in the previous section, cross-coupling methods can be employed to control the linkage position when an aromatic-aromatic bond is formed. Therefore, they are very helpful in preparing various polymers with precisely controlled linkage positions. By applying the various cross-coupling methods to generate π-conjugated polymers consisting of a variety of aromatic compounds, regioregular homopolymers and alternating copolymers can be produced easily; they are difficult to create using traditional oxidative polymerization or electrochemical oxidative polymerization methods. Various π-conjugated polymers have greatly contributed to the development of optical materials, electronic and photovoltaic devices, etc. [88–98] (For recent reviews, see: [99–119]). In this section, recent research on π-conjugated polymers developed using cross-coupling reactions is described, concentrating on their applications to field effect transistors (FETs), solar cells, and light emitting diodes (LEDs).

An FET is a transistor that controls the current between source and drain terminals through a voltage applied to a gate electrode. This voltage establishes a gate in the flow of electrons or holes using an electric field in a channel. These features enable FETs to be used as switching devices, amplifying elements, etc. Since FETs have a planar structure, they are easy to prepare and integrate. Therefore, they are indispensable elements in the integrated circuits currently used in electronic devices. Recently, extensive research on the creation of new π-conjugated polymers that can be used as low-cost electronic materials has been conducted (For recent reviews, see: [120–123]). In particular, development of materials that show higher mobility of holes and electrons has been emphasized.

The p-type semiconducting π-conjugated polymers are used to form a hole-transportation layer. The rapidly growing range of conducting polymers that show field-effect mobilities exceeding 0.1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ is contributing to improvement in basic device performance. For many years, it appeared difficult to achieve such high mobilities with π-conjugated polymers other than regioregular poly-3-hexylthiophene (P3HT) [124, 125]. However, π-conjugated polymers containing various units have since been developed widely. More recently, the semiconducting polymers with mobility values exceeding 1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ have been reported.

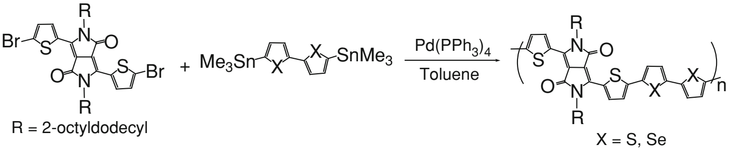
Diketopyrrolopyrole (DPP) has a planar bicyclic structure that leads to a strong π–π interaction. Therefore, π-conjugated polymers containing DPP as a co-monomer unit are expected to be high-performance organic semiconductors. Recently, several DPP-containing alternating π-conjugated polymers have been developed, and their transistor properties were elucidated.

Li et al. reported that an alternating copolymer of DPP and oligothiophene could be synthesized using the Migita-Kosugi-Stille coupling polymerization (Eq. 8.37) and that the copolymer showed a high hole mobility of 0.89 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$. After annealing of the polymer at 100 °C, the hole mobility was increased to 0.97 cm^2 V^{-1} s^{-1} [126, 127].



(8.37)

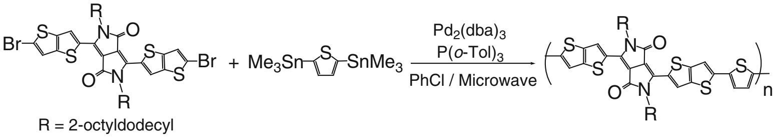
Choi et al. synthesized DPP-based alternating donor-acceptor type copolymers using the Migita-Kosugi-Stille coupling reaction (Eq. 8.38) [128].



(8.38)

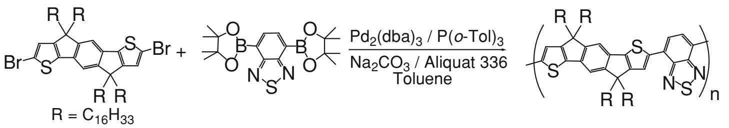
They reported that these polymers showed hole mobilities of *ca.* 0.6 cm^2 V^{-1} s^{-1}. The mobility of one polymer (X=S) was enhanced after annealing at 150 °C to 1.04 cm^2 V^{-1} s^{-1}, and that of another polymer (X=Se) was increased to 1.5 cm^2 V^{-1} s^{-1} after annealing at 180 °C.

Bronstein et al. prepared alternating copolymers consisting of DPP and thieno[3,2-*b*]thiophene using the Migita-Kosugi-Stille coupling reaction (Eq. 8.39) [129]. This polymer showed very high hole mobility of 1.95 cm^2 V^{-1} s^{-1} with no high-temperature annealing.



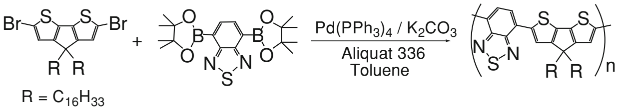
(8.39)

Other polymers with high hole mobilities have also been developed by several groups. Zhang et al. synthesized alternating copolymers consisted of indacenodithiophene and benzothiadiazole using the Suzuki-Miyaura coupling polymerization (Eq. 8.40). This copolymer also showed a high hole mobility of *ca.* 1.0 cm^2 V^{-1} s^{-1} [130].



(8.40)

Müllen et al. reported that alternating copolymers consisting of 2,1,3-benzothiadiazole and a cyclopentadithiophene derivative were synthesized using the Suzuki-Miyaura coupling polymerization (Eq. 8.41) [131] and exhibited a very high hole mobility of 3.3 $cm^2\ V^{-1}\ s^{-1}$ [132, 133].

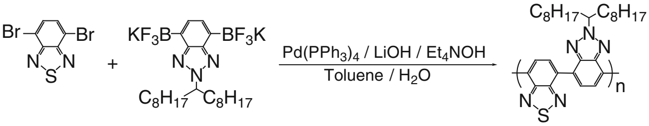


(8.41)

These values are among the highest values obtained from a homogeneous polymer system.

The π-conjugated polymers in which all the unit(s) are formed by electron-accepting monomers are expected to show interesting physical and chemical properties as optoelectronic devices. Since these polymers show features of n-type semiconductors, they are expected to function as an electron-transporting material [134–136]. However, examples of the preparation of such polymers are limited [137–140]. Because it is difficult to make polymers composed only of electron-withdrawing units using oxidative polymerization methods, cross-coupling polymerization methods are particularly useful for producing such polymers.

Ober et al. reported a new class of π-conjugated polymers composed only of electron-accepting monomers prepared using the Suzuki-Miyaura cross-coupling polymerization (Eq. 8.42) [141].

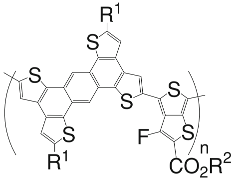
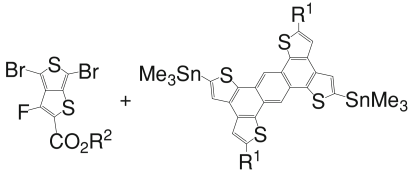
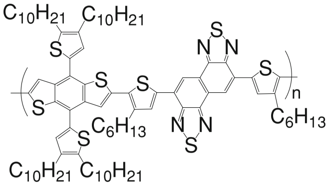
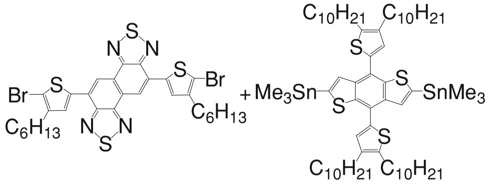
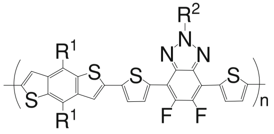
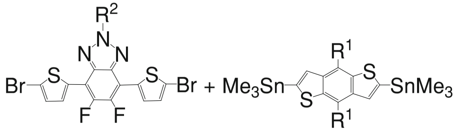
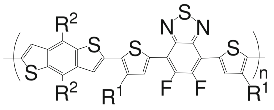
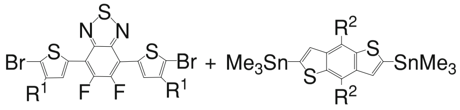


(8.42)

This polymer showed a high electron mobility of $\mu_e = 2 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$. This is the first example of a π-conjugated polymer composed only of electron-accepting units synthesized using the Suzuki-Miyaura coupling. Cross-coupling polymerization methods are very useful in the development of n-type FET materials.

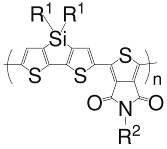
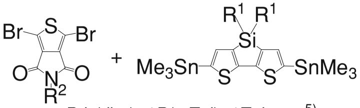
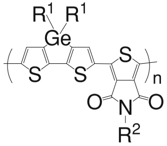
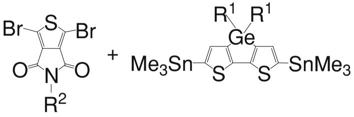
Bulk-heterojunction solar cells (BHSCs) are more cost-effective than inorganic devices, making them an attractive altenative. Since BHSCs were discovered in 1995 [142–144], photovoltaic (PV) devices based on conjugated polymers have attracted much interest. With further development of solar cells using conducting polymers the structures and manufacturing processes of the cells could be further simplified beyond those of the current dye-sensitized solar cells (DSSC). The main disadvantages associated with organic photovoltaic cells are low power conversion efficiency (PCE), low stability, and low strength compared to inorganic photovoltaic cells. Previously, conducting-polymer-based solar cells showed very low PCEs of 10^{-2}–10^{-1} % [145, 146]. The discovery of photoinduced electron transfer in composites of conducting polymers as donors and buckminsterfullerene and its

Table 8.1 Recent development of alternating copolymers for solar cells

Structure	Preparation method	PCE$_{av}$ (PCE$_{max}$)/%
 R^1 = 2-butyloctyl R^2 = 2-ethylhexyl	 $Pd(PPh_3)_4$ / Toluene / DMF	5.6 [170]
	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / toluene	6.00 [171]
 R^1 = 3-butylnonyl R^2 = 2-butyloctyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / *o*-Xylene	6.81 (7.10) [172]
 R^1 = 2-ethylhexyl R^2 = 3-butylnonyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / *o*-Xylene / microwave	6.9 (7.2) [173]

(continued)

Table 8.1 (continued)

Structure	Preparation method	PCE$_{av}$ (PCE$_{max}$)/%
 R^1 = 2-ethylhexyl R^2 = octyl	 $Pd_2(dba)_3$ / $P(o\text{-}Tol)_3$ / Toluene[5)] $Pd(PPh_3)_4$ / Toluene / DMF[6)]	6.6 [174] 7.3 [175]
 R^1 = 2-ethylhexyl R^2 = octyl	 $Pd_2(dba)_3$ / $P(o\text{-}Tol)_3$ / Toluene	7.3 [174]

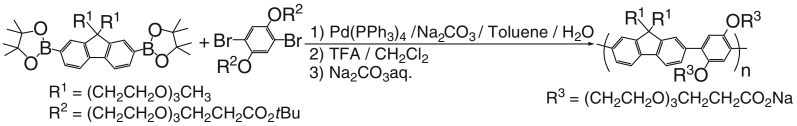
derivatives as acceptors [147] provided a molecular approach to high-efficiency photovoltaic conversion [148, 149]. Since then, many bulk heterojunction polymer solar cells have been developed using π-conjugated polymers containing various monomer units (For recent reviews, see: [150–169]).

In recent years, solar cells using conducting polymers that exhibit high PCEs exceeding 6 % have been developed. Table 8.1 shows recently reported high-PCE-producing π-conjugated polymers prepared by cross coupling polymerization methods.

More recently, Mitsubishi Chemical developed an organic thin film solar cell that used for benzoporphyrin as a p-type organic semiconductor in which the PCE exceeded 10 % [176]. This value is comparable to those of thin-film-type silicon solar cells, which have the highest PCE values in the world. Since polymer-based organic thin film solar cells have the merits quoted above, improvements in high-performance photovoltaic devices through further improvement of the PCE are expected.

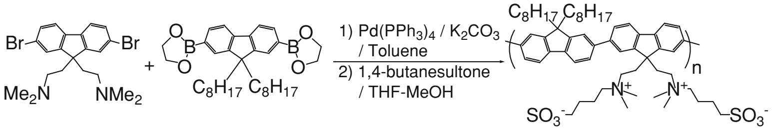
The first polymer light-emitting diode (PLED) composed of π-conjugated polymers was produced in 1990 [177]. Since then, versatile classes of conjugated polymers have been prepared and diverse synthetic methods have been developed (For recent reviews, see: [178–180]). These days, development of new materials that focuses on the luminescence response time is progressing rapidly.

In recent years, conjugated polyelectrolytes have attracted much attention for PLED applications, because they function as electron injection layers (EIL) efficiently and effectively [181–187]. Nguyen et al. reported that a fluorene-phenylene alternating copolymer with an ion-conducting polyethylene pendant was prepared using the Suzuki-Miyaura polymerization (Eq. 8.43) [188] and that this polymer could be used as an EIL in PLEDs [189]. As a result, a fast luminescence temporal response time (200 μs) can be achieved.



(8.43)

Huck et al. reported the preparation of a zwitterionic conjugated polyelectrolyte that had cationic ammonium and anionic sulfonate units in the same side chain (Eq. 8.44). They used this polymer as an EIL and succeeded in creating a high-performance PLED that showed a very fast-response time of less than 10 μs [190].



(8.44)

8.6 Summary

A wide variety of metal-catalyzed cross-coupling reactions has been developed, and a huge number of polymers for functional materials of various natures have resulted from this methodology. Cross-coupling polymerization methods are applicable to the synthesis of varied polymers using diverse monomer materials. Furthermore, since the linkage position between the monomer units is strictly controllable by the design of the monomer(s), regioregular polymers can be invented easily. The methods have distinct potential in the preparation of π-conjugated polymers, since couplings between aryl, alkenyl, and alkynyl species are the most successful confirmed reactions. It is fully expected that these polymerization methods will play a role in the development of not only π-conjugated polymers but also various polymers for functional materials, thus greatly contributing to the development of the material chemistry field.

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