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Accounts

Recent Advances in Phenoxy-Based Catalysts for Olefin Polymerization

Yasuhiko Suzuki, Hiroshi Terao, and Terunori Fujita*

R&D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura-City, Chiba 299-0265

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Olefiin polymerization behavior of phenoxy-based catalysts has been discussed. Phenoxy-based olefin polymerization catalysts are capable of showing high catalytic activities. Moreover, the phenoxy-based catalysts can display unique catalytic properties and thus have offered opportunities to make polyolefinic materials that are difficult or impossible to prepare using conventional catalysts. Therefore, the phenoxy-based catalysts have opened up a new dimension in the fields of olefin polymerization catalysis and polymer synthesis.

Polyolefins such as polyethylene (PE) and polypropylene (PP) are the most widely used polymers in the world today. More than 40 million tons of polyolefins are manufactured every year using transition metal-based catalytic technology. Applications for these polyolefins include food-packaging film and containers, waste-disposal bags, can liners, toys, appliances, and many others such as foam, film, and molded parts, and so forth because of their cost effectiveness as well as low density, strength, and resistance to chemical attack. Additionally, the polyolefins are finding their way into the market to replace common materials such as glass, paper, metal, wood, and concrete. Accordingly, polyolefins are the fastest-growing segment of the polymer industry in spite of the size and the commodity nature of the business.

Although multi-site Ziegler–Natta catalysts have been the workhorses of the polyolefin industry, single-site catalysts represented by metallocene catalysts and constrained-geometry catalysts (CGC) are gaining an increasing presence in the worldwide polyolefin market. The key feature of single-site catalysts is their well-defined active sites in contrast to multi-site Ziegler–Natta catalysts; the former offers an advantage of control over polymer molecular weight and molecular weight distribution, uniform comonomer incorporation, and precise control of polymer stereoregularity.[1–9] With these advantages, single-site catalysts have been used to create quite a few high-performance polyolefins with unique microstructures and a wide spectrum of properties (e.g., linear low-density PE, isotactic and syndiotactic PP (iPP and sPP), stereoblock polypropylene, syndiotactic polystyrene (PS), ethylene/styrene interpolymers (ESI), cyclic olefin copolymers (COC), and polyolefinic elastomers). Consequently, single-site catalysts have had a significant impact on contemporary polyolefin science and technology.

While metallocene catalysts and CGC have been in the forefront of these developments, there has been tremendous interest in the development of high-performance single-site catalysts in both industrial and academic research laboratories. Central to these developments has been the design of a ligand whose steric and electronic properties can readily be modified by the appropriate choice of substituents on the ligand framework. Examples of successful single-site catalysts are many: diimine ligands (with Ni, Pd, and Cu),[10,11] phenoxy–imine ligands (with Ni, V, Cr, Ti, Zr, and Hf), diimine–pyridine ligands (with Fe and Co),[12,13] diamide ligands (with Ti and Zr),[14–16] diamide–ether ligands (with Ti, Zr, Hf),[17] diamide–amine ligands (with Ti, Zr, Hf),[18] phosphine–imide ligands (with Ti),[19] bis(phenoxy–amine) ligands (with Ti, Zr, Hf), bis(phenoxy)–thioether ligands (with Ti, V), tris(pyrazolyl)borate ligands (with Ti),[20] pyrrolide–imine ligands (with Ti, Zr, and Hf),[21,22] indolide–imine ligands (with Ti),[23] phenoxy/imido ligands (with V), phenoxy/cyclopentadienyl ligands (with Ti), amidinate/cyclopentadienyl ligands (with Zr),[24] quinoline–cyclopentadienyl ligands (with Cr),[25] anilide–tropone ligands (with Ni),[26] and amide–pyridine ligands (with Ti, Zr).[27] Many of these catalysts exhibit activities rivaling those of metallocene catalysts and CGC. Moreover, some of the catalysts have provided extraordinary opportunities to synthesize polymers with various microstructures (e.g., hyper-branched polymers, polar monomer copolymers, and polyolefinic block copolymers) that were previously unavailable through other means of polymerization. Therefore, the development of high-performance single-site catalysts has been achieved at a rapid pace, as has been reviewed or commented upon elsewhere.[28]

Among the recently-developed single-site catalysts, phenoxy-based catalysts constitute an important class of olefin polymerization catalysts. Such complexes can indeed produce a variety of polymers (See: Summary, Table 2), some of which are difficult or impossible to prepare using conventional catalysts. For example, phenoxy-based catalysts are capable

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of creating vinyl-terminated low molecular weight PE, functionalized PE and cyclic olefin copolymers, well-defined multimodal PE, ultra-high molecular weight ethylene/α-olefin copolymers, ethylene-styrene alternating copolymers, regio- and stereo-irregular high molecular weight PP and poly(1-hexene), and high molecular weight amorphous propylene/α-olefin copolymers, etc. In addition, some of these complexes can carry out highly-controlled living polymerization of ethylene as well as highly-stereospecific living polymerization of propylene or 1-hexene, and can thus produce high molecular weight monodisperse PE, highly-syndiotactic monodisperse PP, and highly-isotactic monodisperse poly(1-hexene). Moreover, some are able to create unique diblock and multiblock copolymers such as PE-*b*-EPR, sPP-*b*-EPR, poly(1-hexene)-*b*-poly(1-octene) and PE-*b*-EPR-*b*-sPP. Furthermore, specifically designed phenoxy-based catalysts are capable of producing monodisperse polymers catalytically by combining with chain transfer agents, opening up a new methodology for the catalytic production of block copolymers and functionalized polyolefins.

The success of phenoxy-based catalysts clearly depends on the high potential of phenoxy donors as ligands for olefin polymerization catalysts; such potential may result from the electronically flexible nature of phenoxy donors. The unique polymers arising from phenoxy-based catalysts have potential uses for a broad spectrum of applications because of their distinctive microstructures and related material properties. Hence, the recent emergence of phenoxy-based transition metal polymerization catalysts has introduced a new dimension in the field of olefin polymerization catalysis and polymer synthesis.

In this review, we survey recent advances in the area of olefin polymerization catalysis of metal complexes having phenoxy-based ligands [e.g., phenoxy–imine, phenoxy–amine, phenoxy–thioether, phenoxy/cyclopentadienyl, phenoxy–diazene, phenoxy–pyridine, phenoxy–ether, and phenoxy–phosphine]. The goal of this work is not to be a comprehensive review of such complexes, but to highlight their olefin polymerization behavior to demonstrate the high potential of this class of catalysts for creating various polyolefinic materials. This review covers the scientific literature from the mid-1980s to the present regarding olefin polymerization catalysis of phenoxy-based catalysts. Since important discoveries and related information from industrial laboratories appear in the patent literature, a number of patents are included at our discretion in order to provide further information to the readers.

In general, metal complexes are classified according to the metal, since the metal is the center of catalysis. We, however, postulate that ligands play the predominant role in polymerization catalysis and that electronically flexible ligands give highly-active catalysts as long as a potential active-species possesses appropriate electron deficiency as well as a pair of available *cis*-located sites for polymerization (*ligand-oriented catalyst design concept*).[29,30] Therefore, the complexes introduced in this review have been categorized according to the characteristics of their phenoxy-based ligands; namely (i) the donor-atom number of a ligand (A: Monodentate, B: Bidentate, C: Tridentate, D: Teradentate) (ii) the ligand charge (Monoanionic, Dianionic) (iii) the nature of the donor atoms including the formal charge (e.g., [O$^-$, N], [O$^-$, S, O$^-$]) and, if necessary, (iv) the name of the donor functionality (e.g., Phenoxy–Imine, Bridged Bis(Phenoxy–Amine)). For example, bis(phenoxy–imine) Ti complexes are discussed in the section of (B) Bidentate Ligands/(1) Monoanionic Ligands/(1) [O$^-$, N]/(2) Phenoxy–Imine Ligands: Section B.1.1.2. Catalytic activities are introduced as reported in the literature since they are clearly condition dependent (e.g., temperature, monomer concentration (pressure), time, the reactor employed, stirring rate). However, to provide the reader with the qualitative image of catalyst efficiency relative to other catalyst systems, activities are described as high, moderate or low in the text depending on the converted activity values expressed in units of g- or kg-polymer/mmol-cat•h/atm; high (>500 g/mmol-cat•h•atm), moderate (500–100 g/mmol-cat•h•atm) and low (<100 g/mmol-cat•h•atm). Unless otherwise stated, activity values in the text were obtained under atmospheric pressure conditions.

I. Polymerization Behavior

Phenoxy-based ligands have the advantageous properties of diversity as well as tunability. This is because phenol derivatives have rich inventories of commercially available compounds. In addition, a wide variety of substituents (both hydrocarbon- and heteroatom-based substituents) can be introduced in generally good to high yields. As such, phenoxy-based ligands are readily tailored synthetically from both an electronic and steric point of view and thus they possess a wide range of catalyst design possibilities. Therefore, the last few years have seen considerable interest in the development of high-performance catalysts for olefin polymerization using phenoxy-based ligands.

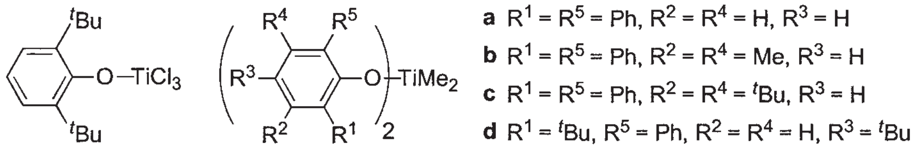
A. Monodentate Ligands. Metal complexes having monodentate phenoxy ligands have been examined less frequently as olefin polymerization catalysts compared to those with bi- or tridentate phenoxy-based ligands. Recently, combination of a phenoxy ligand and a Cp or an arylimido ligand has been revealed to result in unique catalytic behavior of the resultant catalyst.

1. [O$^-$] Phenoxy Ligands. Although synthetic methods for group 4 transition metal complexes with phenoxy ligands were established by Rothwell et al.[31] and Nakamura et al.,[32] only a few applications as catalysts for olefin polymerization had been reported until recently.

The ability of Zr, Hf and Ta complexes incorporating bis(phenoxy) or tris(phenoxy) ligands to mediate olefin polymerization was investigated by Canich.[33] She described how, in association with MAO, these complexes can be active catalysts for the polymerization of ethylene and α-olefins.

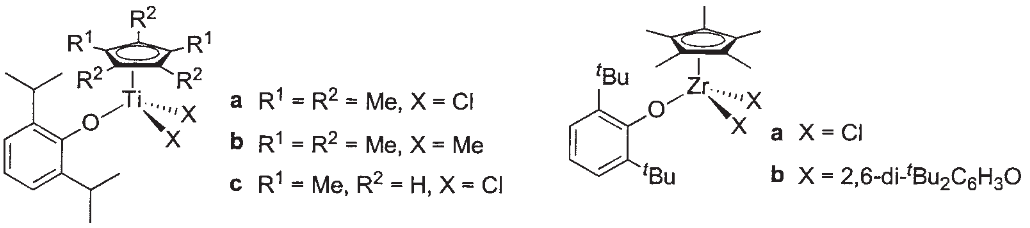
Aaltonen and Seppälä subsequently investigated the ethylene/styrene copolymerization behavior of a Ti complex **1** (Fig. 1) with a phenoxy ligand.[34] They reported that attempted copolymerization of ethylene with styrene using **1**/MAO results in the generation of a mixture of PE and atactic PS. The formation of two kinds of homopolymers suggests the presence of at least two catalytically active species and/or different polymerization mechanisms for ethylene and styrene. No homopolymerization results were described.

Olefin polymerization behavior of Ti complexes **2** having



1 **2**

Fig. 1.



3 **4**

Fig. 2.

bis(phenoxy) ligands was recently discussed by Thorn and Rothwell.[35] These complexes, when activated by $B(C_6F_5)_3$, catalyze the polymerization of ethylene and propylene with low activities (2–6 g-polymer/mmol-cat•h, 0 °C). A correlation between ligand bulk and product molecular weight was found. The atactic PPs obtained are produced through 1,2-insertion/β-hydrogen elimination pathways.

Nomura et al. made seminal contributions to the field of phenoxy-ligated transition metal complexes for olefin polymerization.[36–43,46,47] They reported that Ti(IV) complexes **3** (Fig. 2) coupled with both a phenoxy and a Cp ligand can be a remarkable catalyst for the (co)polymerization of ethylene, α-olefins and styrene. Upon activation with MAO or ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ these complexes polymerize ethylene with high productivity. They investigated the effects of substituents in both the phenoxy and the Cp ring on catalytic properties. The introduction of electron-donating substituents to the Cp ring results in enhanced catalytic activity probably because more electron-donating Cp stabilizes an active species more efficiently. In addition, the presence of bulky substituents is a requirement for high activity. The bulky substituents are thought to provide steric protection to avoid attack of the cocatalyst on the phenoxy-oxygen. Among the complexes examined, **3a** combined with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ displays the highest activity (2.22 kg-PE/mmol-cat•h, 60 °C, 0.4 MPa).[36] The activity is far higher than those obtained from Cp*TiCl$_2$ and (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$TiCl$_2$ under identical conditions, clearly indicating the combination effect of a phenoxy and a Cp ligand.

The success of these complexes is not limited to the polymerization of ethylene. Complex **3** with MAO polymerizes propylene and higher α-olefins (i.e., 1-hexene, 1-octene and 1-decene) with moderate to high activities to afford high molecular weight polymers with narrow molecular weight distributions (e.g., propylene 568 g-PP/mmol-cat•h, 60 °C, 0.4 MPa, M_w 148000, M_w/M_n 1.9: 1-decene 1.04 kg-polymer/mmol-cat•h, 25 °C, M_w 688000, M_w/M_n 1.65).[36,37]

In addition, they showed that **3b** combined with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ displays a very high activity of 5.71 kg-polymer/mmol-cat•h in 1-hexene polymerization at −30 °C when **3b** is pre-treated with ^{i}Bu$_3$Al. Interestingly, the relationship between M_n and the amount of 1-hexene consumed suggested that the catalyst system may have the characteristics of a living 1-hexene polymerization under the conditions examined.[40]

These complexes are also high-performance catalysts for ethylene/α-olefin copolymerization. For instance, **3** in association with MAO copolymerizes ethylene with 1-hexene displaying higher activities than CGC, to give narrow molecular weight distribution copolymers having high 1-hexene contents (e.g., **3a** 263 kg-polymer/mmol-cat•h, 40 °C, ethylene 0.7 MPa, 1-hexene content 38.1 mol %, M_w 337000, M_w/M_n 1.87).[41] The high incorporation ability for α-olefins can probably be attributed to the open nature of the catalyst active sites. Nomura et al. revealed that the Cp ligand employed affects the monomer sequence distributions and the monomer reactivity ratios, which are originally different from those for CGC under the same conditions. These unusual observations may be associated with the flexible internal rotation of both the phenoxy and the Cp ligands of the complexes.

Furthermore, when treated with MAO, these complexes were shown to be effective catalysts for styrene polymerization as well as ethylene/styrene copolymerization.[42,43] For example, **3c** exhibits a very high activity of 4.27 kg-PS/mmol-cat•h and yields high molecular weight sPS (25 °C, M_w 283000, M_w/M_n 1.83). Notably, **3c** with MAO promotes the copolymerization of ethylene and styrene with high activity (4.45 kg-polymer/mmol-cat•h, 25 °C) and forms a copolymer having a significantly high styrene content (styrene content 56.6 mol %, M_w 116000, M_w/M_n 1.96). The ethylene/styrene copolymer contains head-to-tail sequences, which are not detected in the copolymers arising from CGC, suggesting that the catalyst system efficiently incorporates styrene into a growing polymer chain.

The analogous Zr complexes **4** were examined by Antiñolo and Otero as ethylene polymerization catalysts.[44] They reported that complex **4a** in combination with MAO displays ethylene polymerization activities (max. 4.26 kg-PE/mmol-cat•h, 29 °C, 0.35 MPa) comparable to that observed for Cp$_2$ZrCl$_2$. Complex **4b** with tris(phenoxy) ligands shows poor catalyst performance when treated with MAO.

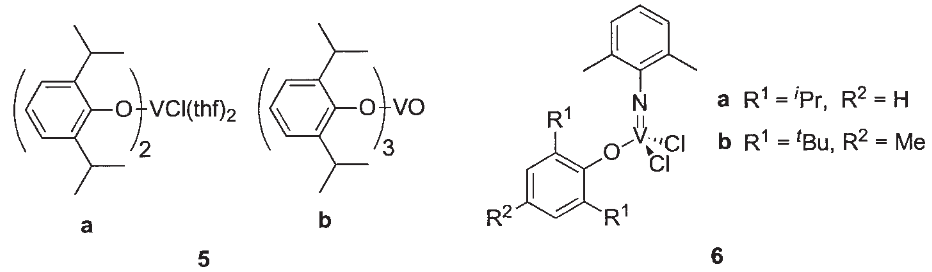


Fig. 3.

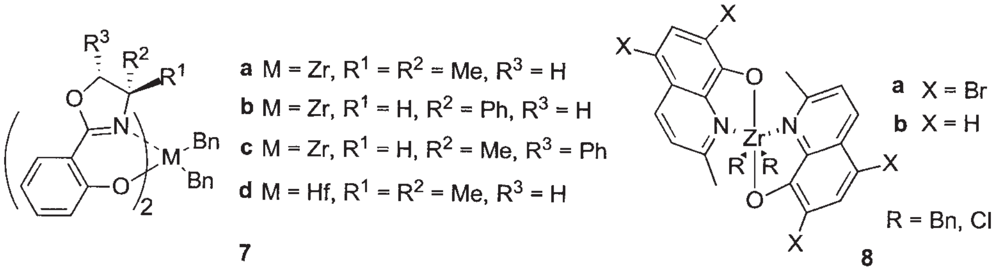


Fig. 4.

While the majority of metal complexes with monodentate phenoxy ligands reported so far contain group 4 transition metals, some phenoxy-ligated V complexes have recently been developed. Henderson and Sobota studied bis(phenoxy) and tris(phenoxy) V complexes **5** (Fig. 3) for olefin polymerization.[45] Complexes **5** in combination with $MgCl_2/Et_2AlCl$ are highly-active catalysts for the polymerization of ethylene (max. 12.4 kg-PE/mmol-cat•h, 0.6 MPa). The researchers also described that the catalyst systems display high activities in the copolymerization of ethylene with 1-hexene (>5 kg-polymer/mmol-cat•h).

Recently, Nomura et al. expanded the phenoxy-ligated Ti chemistry into V complexes.[46,47] They studied the catalytic behavior of V complexes **6** with a phenoxy and a phenylimido ligand for olefin polymerization as well as ring-opening metathesis polymerization of norbornene. In the presence of MAO, **6** exhibits a high activity for ethylene polymerization and forms high molecular weight PE (max. 967 g-PE/mmol-cat•h, 25 °C, 0.8 MPa, M_w 2030000, M_w/M_n 2.73). Additionally, **6**/MAO sysytem produces atactic unimodal PP and poly-1-hexene (PP: 4.02 g-PP/mmol-cat•h, M_w 245000, M_w/M_n 2.01, poly-1-hexene: 2.03 g-polymer/mmol-cat•h, M_w 81100, M_w/M_n 1.69): both polymers contain 2,1- as well as 1,2-inserted units. Notably, **6** combined with Et_2AlCl displays much higher ethylene polymerization activity (>8.22 kg-PE/mmol-cat•h, 25 °C, 0.8 MPa ethylene pressure) than the MAO activation system. In addition, **6** with Me_3Al is shown to initiate ring-opening metathesis polymerization of norbornene (TON 22, 25 °C, M_n 49600, M_w/M_n 2.04). A series of papers by Nomura and co-workers demonstrate that the combined use of a monodentate phenoxy ligand and another robust ligand in transition metal complexes can create remarkable olefin polymerization catalysts.

B. Bidentate Ligands. Among phenoxy-based complexes, metal complexes bearing bidentate phenoxy-based ligands [e.g., phenoxy–imine, phenoxy–Cp, and bis(phenoxy)] have been extensively studied as olefin polymerization catalysts, leading to a variety of successful catalysts. The development of such complex catalysts has contributed enormously to the recent progress of olefin polymerization catalysis and polymer synthesis.

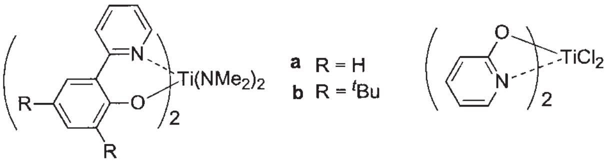
1. Monoanionic Ligands. 1.1. [O^-, N]. 1.1.1. Phenoxy–Oxazoline/Quinoline/Pyridine/Diazene/Amine. Pioneering research on the structural properties and ethylene polymerization behavior of [O^-, N] ligated group 4 transition metal complexes has been made by Floriani et al. and Jordan et al. Cozzi and Floriani studied Zr and Hf complexes **7** (Fig. 4) bearing phenoxy–oxazoline ligands, which are readily prepared and easily modified using commercially available compounds.[48] A cationic complex generated from **7** and $HNEt_3BPh_4$ works as a catalyst for the polymerization of ethylene without the need for a cocatalyst albeit at a low rate (0.12 g-PE/mmol-cat•h). Molecular structures of a cationic complex/THF adduct as well as a neutral complex were established by X-ray crystallographic analyses. In this connection, Johnson et al. prepared Ni complexes incorporating phenoxy–oxazoline ligands for olefin polymerization.[49]

Bei and Jordan investigated the structures and ethylene polymerization properties of Zr and Hf complexes featuring phenoxy–quinoline (8-quinolinolato) ligands (**8**).[50] Single-crystal X-ray analysis revealed that in the solid state these complexes possess approximately octahedral metal centers with a *trans*-O, *cis*-N, and *cis*-R ligand arrangement. NMR studies established that these complexes and their corresponding cationic complexes undergo inversion of metal configuration in solution ($\Delta G^{\#}$: neutral complexes 15–18 kcal/mol, cationic complexes >20 kcal/mol), suggesting the fluxional character of these complex systems. The potentially fluxional character of a group 4 transition metal complex with two non-symmetric ligands is probably related to some of the unique catalytic properties displayed by two non-symmetric-ligand ligated group 4 transition metal complexes (e.g., multimodal polymer formation, sPP production with C_2-symmetric catalysts). Upon treatment with $HNMe_2PhB(C_6F_5)_4/{}^iBu_3Al$, complexes having brominated ligands are active for ethylene polymerization (max. 41 g-PE/mmol-cat•h), whereas those with non-brominated ligands are inactive. These observations are consistent with the proposal that electron-withdrawing Br substituents increase the degree of unsaturation associated with the cationic active species and thus enhance the reactivity towards ethylene. This represents the first report on a correlation between electronic properties of a non-metallocene complex and catalytic activity. It is worth noting that, for these systems, electron-withdrawing substituents are preferable for polymerization activity, though electron-donating substituents normally increase the polymerization activity of group 4 metallocene catalysts. Regarding [O, N] ligand systems, Tsukahara, Kim, and Jordan also studied Ti and Zr complexes containing alkoxy–pyridine ligands.[51,52]

Inoue and Fujita reported on a phenoxy–pyridine ligated Ti complex **9** (Fig. 5) that shows high catalytic activities in ethylene polymerization (max. 564 g-PE/mmol-cat•h) when activated by ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$.[53] It should be noted that introduction of a bulky substituent *ortho* to the phenoxy-oxygen has practically no effect on activity. DFT calculations suggested that an ethylene-coordinated active species derived from **9** unexpectedly adopts a structure with a *trans*-N and *cis*-O ligand arrangement. It is likely that a substituent *ortho* to the phenoxy-oxygen is not effective for steric protection of the Ti center and for ion separation between the cationic Ti center and anionic cocatalyst.

Highly-active Ti complexes possessing phenoxy–pyridine (2-hydroxypyridine) ligands were disclosed by Nagy et al., who reported that **10** combined with MAO displays high ethylene polymerization activity (8.8 kg-PE/mmol-cat•h, 80 °C, 1.03 MPa).[54]

Hagen and van Koten synthesized V complexes **11** (Fig. 6) bearing phenoxy–amine ligands as ethylene/propylene copolymerization catalysts.[55] Upon activation with Et$_{1.5}$AlCl$_{1.5}$, these complexes are capable of copolymerizing ethylene and propylene to produce high molecular weight copolymers (e.g., **11a** 159 g-polymer/mmol-cat•h, M_w 670000, propylene content 37.5 mol %). They described a related V complex **11c** with a phenoxy–diamine ligand showing much lower activity than the phenoxy–amine ligated complexes.



9 **10**

Fig. 5.

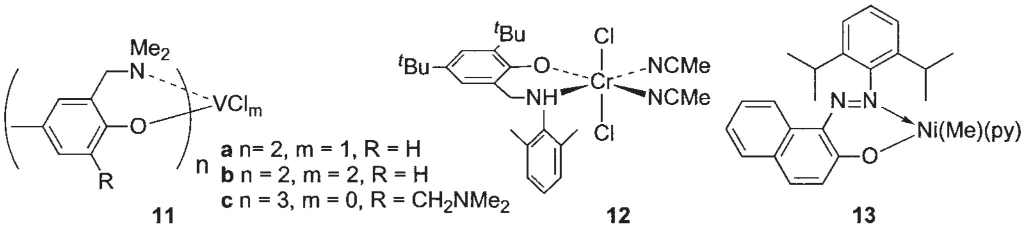
A distorted octahedral Cr complex **12** having a phenoxy–amine ligand developed by Gibson and co-workers provides high molecular weight PE having virtually no branching, with an activity of 130 g-PE/mmol-cat•h (M_w 827000, M_w/M_n 9.8) when treated with Et$_2$AlCl. In combination with MAO, **12** is a poor catalyst for ethylene polymerization.[56] Introduction of additional phenoxy–amine ligand to **12** affords a lower activity catalyst.

Neutral Ni complexes **13** incorporating phenoxy–diazene ligands that are activator-free catalysts were developed by Mecking and Keim (See also 1.1.2.4).[57] Although no bulky substituent *ortho* to the phenoxy-oxygen is placed, these complexes are highly-active towards ethylene (max. TOF: 2860, 5 MPa ethylene pressure). Bulky substituents (i.e., isopropyl) on the aryl group bound to the diazene function are a requirement for the formation of PE; otherwise, oligomers are obtained, suggesting the coordination of the diazene moiety to the metal during catalysis.

1.1.2. [O$^-$, N] Phenoxy–Imine. Grubbs, Ittel, Fujita and their co-workers discovered that Ni and group 4 transition metal complexes with phenoxy–imine chelate ligands were a remarkable class of catalysts for the (co)polymerizations of ethylene, α-olefins, and even polar monomers. These discoveries together with phenoxy–imine ligands' ready accessibility and amenability to modification have led to an upsurge of interest in olefin polymerization catalysis of phenoxy–imine-based catalysts. Because of a large number of papers in this area, this section is further divided according to the central metals.

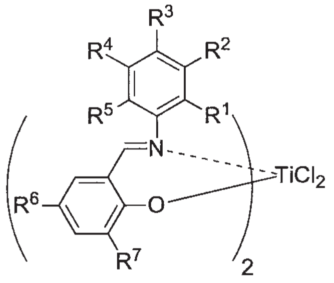
1.1.2.1. Group 4 Metals. One of the recent additions to the highly-active non-metallocene polymerization catalysts are bis(phenoxy–imine) group 4 transition metal complex catalysts. These catalysts were discovered based on a ligand-oriented catalyst design concept at Mitsui Chemicals, which was discussed in detail in a recent review by Makio and Fujita.[30]

1.1.2.1.1. Ti Complexes. Matsui, Fujita and co-workers introduced a new class of Ti complexes bearing phenoxy–imine ligands (Fig. 7) that can be highly active catalysts for the polymerization of ethylene.[58,59] For example, **14a** and **14b** with MAO activation display very high activities and produce high molecular weight linear PEs (**14a**; 3.3 kg-PE/mmol-cat•h, 25 °C, M_v 510000; **14b**, 4.6 kg-PE/mmol-cat•h, M_v 604000). Increasing polymerization temperature from 25 °C to 75 °C gave rise to no significant change in product molecular weight (M_v 546000–440000), which is highly unusual because normally molecular weight decreases with the increase in temperature due to enhanced chain transfer reactions. Interestingly, these Ti complexes possess some characteristics of living ethylene polymerization under limited conditions (for



11 **12** **13**

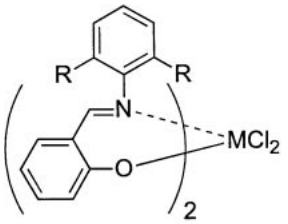
Fig. 6.



14

a $R^{1-5} = R^6 = H, R^7 = {}^tBu$
b $R^{1-5} = R^6 = H, R^7 = Ph$
c $R^1 = R^3 = R^5 = R^7 = H, R^2 = R^4 = F, R^7 = {}^tBu$
d $R^1 = R^5 = R^6 = H, R^{2-4} = F, R^7 = {}^tBu$
e $R^1 = R^3 = R^5 = R^6 = H, R^2 = R^4 = CF_3, R^7 = {}^tBu$
f $R^{1-5} = R^6 = H, R^7 = SiMe_3$
g $R^{1-5} = H, R^6 = R^7 = {}^tBu$
h $R^{1-5} = F, R^6 = H, R^7 = {}^tBu$
i $R^{1-5} = F, R^6 = R^7 = {}^tBu$
j $R^{1-5} = F, R^6 = H, R^7 = SiMe_3$
k $R^1 = R^3 = R^5 = F, R^2 = R^4 = H, R^6 = Me, R^7 = CMe_2Ph$
l $R^1 = F, R^{2-6} = H, R^7 = {}^tBu$
m $R^1 = R^5 = F, R^{2-4} = R^6 = H, R^7 = {}^tBu$
O $R^1 = R^3= R^5 = F, R^2 = R^4 = R^6 = H, R^7 = {}^tBu$

Fig. 7.



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a M = Ti, R = ${}^iPr$
b M = Ti, R = H
c M = Zr, R = ${}^iPr$
d M = Zr, R= H

Fig. 8.

example: **14a**, 1 min polymerization, 25 °C; M_n 52000, M_w/M_n 1.12, 50 °C; M_n 65000, M_w/M_n 1.17, 75 °C; M_n 54000, M_w/M_n 1.20) though they are not applicable to living propylene polymerization and block copolymer formation.[60a,60b,61] Very recently, Coates et al. have confirmed that modified bis(phenoxy–imine)Ti complexes, bis(phenoxy–ketimine)Ti complexes, can also mediate living ethylene polymerization under limited conditions, while the complexes provide relatively low molecular weight PEs with low productivity (for example: 8 min polymerization, 50 °C, M_n 40700, M_w/M_n 1.20).[60c] Michiue and Fujita found that **14a**/MAO converts styrene to highly syndiotactic PS with high efficiency.[62] Molecular structures of the Ti complexes were studied using X-ray analyses as well as DFT calculations.[58,59]

Strauch and Erker also investigated the structural properties and ethylene polymerization behavior of a series of phenoxy–imine ligated Ti and Zr complexes **15** (Fig. 8).[63] Low activities are typically observed (max. 81 g-PE/mmol-cat•h) for these complexes with MAO, probably due to the absence of a bulky *ortho*-phenoxy substituent. Significantly, they showed that the favored coordination geometry of bis(phenoxy–imine) Ti complexes can be controlled by a delicate balance of electronic and steric effects. Complex **15a** has a *cis*-O, *trans*-N, and *cis*-Cl arrangement, conversely complex **15b** missing the two isopropyl groups possesses a *trans*-O, *cis*-N, and *cis*-Cl disposition, indicating that these bis(phenoxy–imine) complexes potentially provide well-defined multimodal polymers.

Ishii and Fujita demonstrated that the electrophilicity of the Ti center in active species plays a dominant role in determining the catalytic activity for bis(phenoxy–imine) Ti complexes.[64] They developed Ti complexes (**14c**–**14e**) possessing multiple F(s) or CF_3(s) in the phenoxy–imine ligand that exhibit very high ethylene polymerization activities (34.8–43.3 kg-PE/mmol-cat•h), exceeding those observed for early group 4 metallocene catalysts under the same conditions.

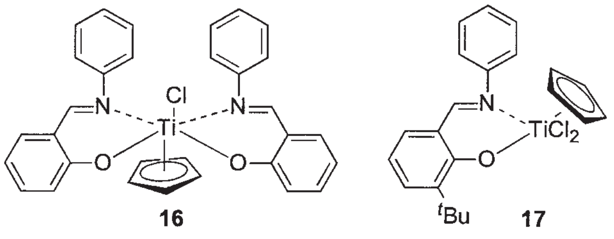
The structure–catalytic performance relationships of phenoxy–imine ligated Ti complexes with MAO catalyst systems were established by Furuyama, Saito, and Fujita.[61,65] For ethylene polymerization, they reported that the steric bulk provided by the substituent *ortho* to the phenoxy-oxygen is fundamental to obtaining both high activity and high molecular weight. In addition, they demonstrated that complexes bearing bulky *ortho*-phenoxy substituents are capable of polymerizing propylene in a stereospecific fashion to form moderately- to highly-syndiotactic PPs. As a result, they developed a Ti complex (**14f**) with a trimethylsilyl group *ortho* to the phenoxy-oxygen that produces highly-syndiotactic PP (0 °C, *rrrr* 84%) with a very high T_m of 140 °C. Microstructural analysis using ^{13}C NMR spectroscopy indicated that the syndiotactic polymers are produced via a chain-end control mechanism regardless of C_2 symmetric catalysts. The formation of sPPs with C_2 symmetric bis(phenoxy–imine) Ti complexes indicates that catalyst symmetry is not a rigid requirement for determining polymer stereochemistry. Chain propagation of this family of complexes was revealed by Saito and Fujita[66] to proceed through a predominant 2,1-insertion of propylene, which will be discussed later. Lamberti and Pellecchia concluded that the solvent employed can affect the syndioselectivity of bis(phenoxy–imine) Ti complexes (e.g., **14a**, 20 °C, 0.27 MPa, toluene: *rr* 87%, heptane: *rr* 62%).[67] Saito and Fujita mentioned that the MAO employed has a significant influence on the syndioselectivity.[61] Moreover, Furuyama, Fujita and co-workers also showed that the attachment of an alkyl substituent to the phenyl group on the imine-nitrogen results in a deleterious effect on catalytic activity and renders the resulting complex practically inactive for propylene polymerization.[61]

Tian and Coates applied combinatorial methods to the screening of stereoselective polymerization catalysts using bis(phenoxy–imine) Ti complexes developed by Fujita and co-workers.[68] They found that in the presence of MAO, a modified complex **14g** forms fairly sPP (0 °C, *r* 94%) with a

T_m of 108 °C via a chain-end-controlled mechanism, among 78 possible complexes containing phenoxy–imine ligands synthesized from the combination of three salicylaldehydes and four anilines. While the combinatorial approach is often viewed by some with skepticism, the results obtained are in perfect accord with the prediction based on the structure–catalytic performance relationships[61] discussed above. Namely, considering the substituent effects on activity and syndioselectivity, one concluded that the most promising candidate for a syndioselective catalyst among the possible 78 complexes is complex **14g**, which is exactly what Coates et al. identified as a stereoselective polymerization catalyst. Thus, the above combinatorial approach can be an effective tool for the discovery of stereoselective polymerization catalysts. It is anticipated that improved catalyst systems will be discovered using similar combinatorial strategies in the near future.

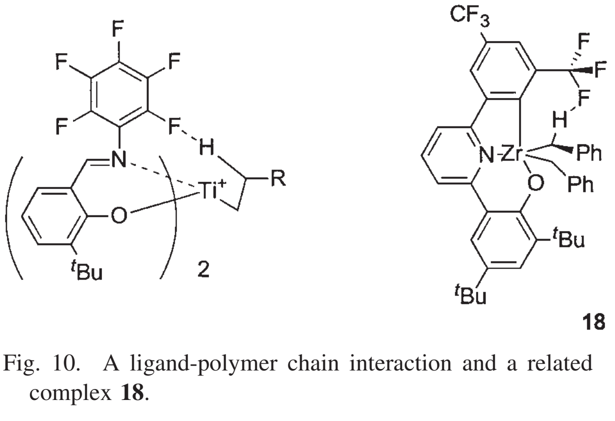
The combined use of a phenoxy–imine ligand and a Cp ligand in Ti complexes (Fig. 9) was reported by Huang and Qian.[69] **16** in conjunction with MAO displays higher catalytic performance than Cp_2TiCl_2 for ethylene homopolymerization and ethylene/1-hexene copolymerization in terms of catalytic activity and product molecular weight (ethylene polymerization; 44 g-PE/mmol-cat•h, M_w 1670000), indicating a high potential of a phenoxy–imine donor as a ligand though no mechanistic details are given. Matsui and Fujita also explored the combination of a phenoxy–imine and a Cp ligand to group 4 transition metal complexes (**17**).[65,70a] Detailed structure and polymerization behavior of **17** was recently reported by Bott, Bochmann, and Lancaster.[70b]

Mitani, Nakano, and Fujita developed a conceptually new strategy for the achievement of controlled living olefin polymerization stemming from an attractive interaction between a ligand and a growing polymer chain (Fig. 10).[60a,71–74] They discovered that fluorinated bis(phenoxy–imine) Ti complexes **14h** combined with MAO can induce highly-controlled living ethylene polymerization as well as highly-syndiospecific chain-end controlled living propylene polymerization above room temperature. For instance, **14h** with MAO activation at 50 °C affords monodisperse PE (M_w/M_n 1.13) having a very high M_n of 424000 with exceptionally high activity (TOF 21500/min/atm). Remarkably, at 75 °C and 90 °C, **14h**/MAO generates PEs with fairly narrow molecular weight distributions (75 °C; M_w/M_n 1.15, M_n 272000: 90 °C; M_w/M_n 1.30, M_n 167000).[60a,72] Moreover, **14h**/MAO promotes room-temperature living propylene polymerization and produces highly-syndiotactic monodisperse PP (M_n 28500, M_w/M_n 1.11, *rr* 87%, T_m 137 °C).[75,76] DFT calculations suggest that an attractive interaction of the fluorine *ortho* to the imine-nitrogen with a β-hydrogen on a growing polymer chain prevents chain transfers, resulting in the realization of highly-controlled living polymerization. The attractive interaction capable of suppressing chain transfers probably sets a standard for controlled living polymerization of simple olefins via insertion chemistry.[60a,71,73–75]



16 17

Fig. 9.



18

Fig. 10. A ligand-polymer chain interaction and a related complex **18**.

Significantly, Kui and Chan have recently demonstrated with NMR as well as X-ray studies the attractive interaction between a fluorine in the ligand and a hydrogen on a benzyl group attached to the central metal for a group 4 transition metal complex (Fig. 10, **18**), potentially indicating the possibility of the attractive interaction between the functionalized ligand and the growing polymer chain.[77] Further research into the attractive interaction of the ligand with the growing polymer chain is expected to result in the discovery of additional hitherto-unknown polymerizations.

The fluorinated bis(phenoxy–imine) Ti complexes are capable of carrying out the living polymerization of both ethylene and propylene, which have thus provided access to both ethylene- and propylene-based block copolymers in addition to monodisperse PEs and syndiotactic PPs (sPPs).[60a,71,72,78,79] With these Ti complexes, Mitani, Mohri and Fujita created a variety of unique diblock and multiblock copolymers such as PE-*b*-EPR, PE-*b*-EPR-*b*-PE, sPP-*b*-EPR, PE-*b*-sPP and PE-*b*-EPR-*b*-sPP,[60a,71,78] most of which were previously inaccessible with Ziegler–Natta catalysts. Kojoh, Matsugi and Fujita demonstrated the considerable potential of sPP-*b*-EPR block copolymers as a compatibilizer using transmission electron microscopy (TEM).[78] Additionally, the unique structure of an individual PE-*b*-EPR molecule and nano-assembly of PE-*b*-EPR molecules were revealed for the first time by Ono, Matsugi and Fujita with atomic force microscopy (AFM).[80]

A modified version of Ti complex **14i**, which has an additional ^{t}Bu group *para* to the phenoxy-oxygen was prepared by Tian, Hustad, and Coates.[81,82] At ambient temperatures, propylene can be polymerized with **14i**/MAO to sPP by chain-end control in a living fashion. Although the complex **14i** was described to be an exceptional catalyst for living propylene polymerization relative to **14h**, Mitani and Fujita reported that **14i** shows practically the same catalytic performance as **14h** under identical conditions (e.g., 25 °C, 5h: **14i**; *rr* 86%, T_m 135 °C, M_n 29800, M_w/M_n 1.15, **14h**; *rr* 87%, T_m 137 °C, M_n 28500, M_w/M_n 1.11).[73,75] This modified complex produced a sPP-*b*-EPR diblock similar to that described above by Kojoh and Fujita.[81] In addition, Fujita and Coates synthesized nearly monodisperse atactic ethylene-cyclopentene copolymers after having isolated, *cis*-1,2-cyclopentane units and PE-*b*-poly(ethylene-*co*-cyclopentene) using the same complex.[83]

Since the fluorinated bis(phenoxy–imine) Ti complexes developed at Mitsui Chemicals are the first examples of living and, at the same time, highly stereoselective catalysts for the polymerization of propylene,[71,78] there has been growing interest in their propylene polymerization catalysis. With chain-end analysis, Saito and Fujita elucidated that syndiospecific propylene insertions occur with predominant 2,1-regiochemistry—a phenomenon never observed for a group 4 metal-based catalyst.[66,73,75] This highly unusual insertion mode can be applied to the synthesis of unique polymers based on diene monomers.[84] Recently, the generality of the 2,1-regiochemistry has been confirmed by Pellecchia et al.[67] and Coates et al.[82] using sophisticated polymerization as well as NMR techniques. More recently, Talarico, Cavallo, and Busico[85] have reported that, based on a theoretical approach, a 1,2-insertion is slightly favored for a 1,2-inserted polymer chain whereas a 2,1-insetion is preferred for a 2,1-inserted polymer chain; this tendency is consistent with the experimental results reported by Fujita et al.[66,73,75] Mitani and Fujita elucidated that the sPPs formed with fluorinated bis(phenoxy–imine) Ti complexes possessed regio-block structures, which are classified into two types: one involving consecutive regioirregular units and the other having isolated regioirregular units.[75]

An exquisitely designed bis(phenoxy–imine) Ti complex created sPPs with unprecedentedly high T_ms. Mitani, Terao and Fujita developed a phenoxy–imine ligated Ti complex **14j** that forms highly-syndiotactic monodisperse PPs (25 °C; *rr* 93%, M_n 47000, M_w/M_n 1.08: 0 °C; *rr* 94%, M_n 24700, M_w/M_n 1.08) with exceptionally high T_ms of 152 °C (25 °C polymerization) and 156 °C (0 °C polymerization).[75,79] The T_m of 156 °C represents the highest T_m value ever observed among sPPs. These results are remarkable in view of the tremendous technological significance of high T_m sPPs. Mitani and Fujita also revealed that, despite a chain-end control mechanism, the steric bulk of the substituent *ortho* to the phenoxy-oxygen controls the syndioselectivity of the polymerization and the sterically bulky substituent results in highly-syndiospecific, thermally robust living propylene polymerization.[75,79] They have given the name "*ligand-directed chain-end control*" to these chain-end controlled polymerizations that are evidently governed by the ligand structures.

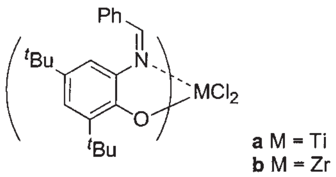
A site-inversion mechanism based on computational studies was proposed by Milano and Cavallo for explaining the formation of sPPs with C_2 symmetric bis(phenoxy–imine) Ti complexes.[86] The key feature of the mechanism is that site-inversion between diastereomeric Λ and Δ configurations is much faster than propylene insertion. The predicted catalytic behavior resulting from the site-inversion mechanism and the experimental results match well. Accordingly, the site-inversion mechanism seems reasonable for the formation of sPPs with the C_2 symmetric Ti complexes at the present time, assuming that the catalytically active species possesses an octahedral geometry with a *trans*-O and *cis*-N disposition.

With the aid of the attractive interaction between the ligand and the polymer chain, fluorinated bis(phenoxy–imine) Ti complexes have achieved some of the crucial objectives concerning living olefin polymerization (i.e., highly controlled living ethylene polymerization, highly syndiospecific living propylene polymerization, and the synthesis of unique block copolymers).[60a,74,75] A crucially important objective remains in this field, however, and that is to realize the catalytic production of monodisperse polymers. Mitani, Mohri, and Fujita have recently succeeded in the catalytic production of monodisperse PEs and Zn-terminated PEs by combining appropriately designed fluorinated Ti complexes **14k** with chain transfer agents (i.e., H_2 and Et_2Zn). These results open up the possibility of the catalytic production of block copolymers and functionalized polymers.[74,87]

It is often observed that the cocatalyst employed has a significant influence on catalytic behavior of a complex for olefin polymerization. Saito and Fujita reported that on activation with ${}^iBu_3Al/Ph_3CB(C_6F_5)_4$ bis(phenoxy–imine) Ti complexes yield ultra-high molecular weight PEs and PPs unlike MAO activation.[59,88] For example, **14a** with ${}^iBu_3Al/Ph_3CB(C_6F_5)_4$ forms PE having an M_v of 5860000 with an activity of 410 g-PE/mmol-cat•h at 50 °C under atmospheric pressure. In addition, this catalyst system produces ultra-high molecular weight atactic PP (M_w 8286000).[88] These molecular weights are some of the highest encountered in homogeneous olefin polymerization catalysts. Though the precise nature of the active species of these systems has not been elucidated, the active species originating from these catalyst systems are proposed to be bis(phenoxy–amine) complexes based on NMR studies.[59,88]

Additionally, unique catalytic behavior of **14a** with ${}^iBu_3Al/Ph_3CB(C_6F_5)_4$ for higher α-olefin polymerization was demonstrated by Saito and Fujita, who showed that the catalyst system favors a 2,1-insertion of a monomer and furnishes high molecular weight [e.g., poly(4-methyl-1-pentene M_w 1400000, poly(1-octene) M_w 950000] atactic poly(higher α-olefin)s with ca. 50 mol % of regioirregular units.[89–91] These are the first examples of regio- and stereo-irregular high molecular weight poly(higher α-olefin)s (*ultra-random polymers*). Because of the good incorporation of 1-hexene comonomer, ethylene/1-hexene copolymers having a wide variety of 1-hexene contents were successfully prepared by **14a**. Remarkably, the system displays higher activities towards higher α-olefins with sterically bulkier substituents (activity order; 4-methyl-1-pentene > 1-decene > 1-octene > 1-hexene).[91] This highly unusual observation can be explained as follows: a sterically bulkier side chain derived from the last inserted higher α-olefin of the growing polymer chain opens the phenoxy–amine ligands wider, which facilitates the higher α-olefin's coordination to the metal and its insertion into the metal–carbon bond. This postulate may provide a new strategy for the design of catalysts with high incorporation ability for sterically bulky monomers.

Nakayama, Bando and Fujita introduced new olefin polymerization catalyst systems composed of bis(phenoxy–imine) Ti complexes **14a**, **14b** and $MgCl_2$-based cocatalysts.[92] The systems exhibit very high catalytic activities (**14a** max. 36.3 kg-PE/mmol-cat•h, 50 °C, 0.9 MPa ethylene pressure) comparable to those obtained with MAO cocatalyst systems and produce (co)polymers with narrow distributions of molecular weight and chemical composition. These results represent



19

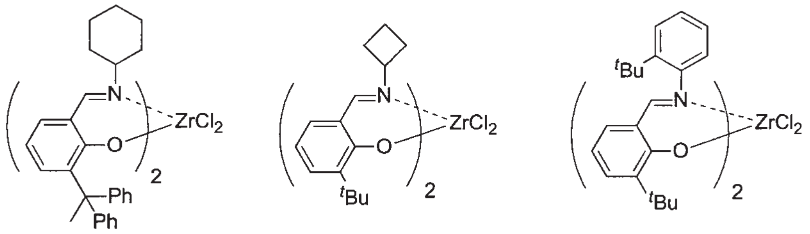
Fig. 11.

the first examples of MAO- and borate-free, highly-active single-site catalyst systems based on a transition metal complex and a $\mathrm{MgCl_2}$-based cocatalyst. Notably, these new single-site catalyst systems are shown to be $\mathrm{MgCl_2}$-supported catalyst systems, suggesting that the systems possess a technological advantage vis-à-vis control over polymer morphology.

New types of phenoxy–imine ligated complexes were introduced by Suzuki and Fujita.[93] They developed Ti and Zr complexes **19** (Fig. 11) with phenoxy–imine ligands that are structurally different from the ligands discussed above, yet contain the same coordination sites. Upon activation with $^{i}\mathrm{Bu_3Al}$/$\mathrm{Ph_3CB(C_6F_5)_4}$, Ti complex **19a** exhibits higher activities at higher temperatures (max. 5.78 kg/mmol-cat•h, 75 °C). They discovered that imine moiety is reduced by $^{i}\mathrm{Bu_3Al}$ to amine function in the catalyst generation process, giving highly active species for ethylene polymerization. Only moderate activities are obtained with MAO activation.

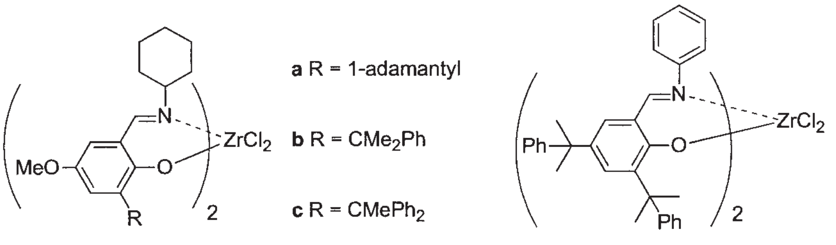
1.1.2.1.2. Zr Complexes. Matsui, Fujita and co-workers demonstrated that bis(phenoxy–imine) Zr complexes **20–26** (Figs. 12–14), **28b** (Fig. 15) can be activated with MAO to give extremely active catalysts for the polymerization of ethylene.[29,65,94–96] The steric bulk provided by the substituent *ortho* to the phenoxy-oxygen plays a pivotal role in achieving high activity. Activity values in many cases are far higher than those seen with early group 4 metallocene catalysts under analogous conditions. The highest activity obtained by **20** reached an astonishing value of 6552 kg-PE/mmol-cat•h at 25 °C under atmospheric pressure, which is two orders of magnitude greater than that of $\mathrm{Cp_2ZrCl_2}$ under identical conditions.[30,97] This activity corresponds to a catalyst turnover frequency (TOF) value of 64900/sec/atm, which is probably the largest of all known catalytic reactions. Generally, the PEs produced are end-capped with vinyl groups, suggesting that β-hydrogen transfer is the predominant chain-termination process.

Substituents on the imine-nitrogen significantly affect product molecular weights. Ishii, Matsuura and Fujita reported that **21** having a cyclobutyl group on the imine-nitrogen generates vinyl-terminated low molecular weight PE (M_w 2100, vinyl selectivity 90%)[98] whereas **22** with a 2-*tert*-butylphenyl group



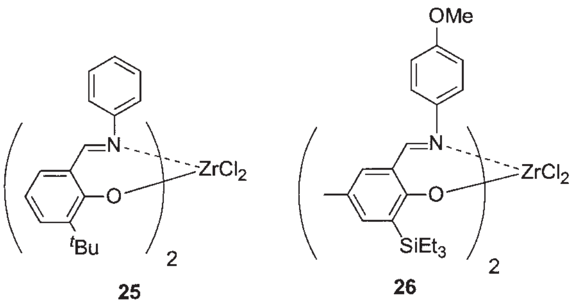
20 **21** **22**

Fig. 12.



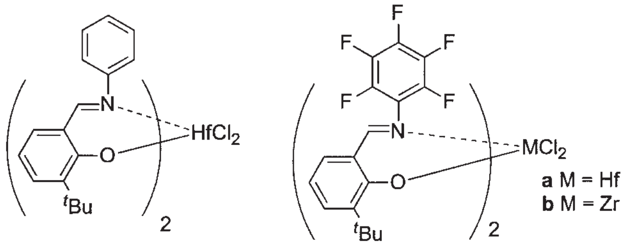
23 **24**

Fig. 13.



25 **26**

Fig. 14.



27 **28**

Fig. 15.

forms markedly high molecular weight PE ($M_v > 2740000$).[96]

Although early bis(phenoxy–imine) Zr complexes had noticeably reduced activities at elevated temperatures, Matsukawa and Fujita developed thermally robust catalysts by elaborate catalyst design work, that exhibit strikingly high activities (3000–9000 kg-PE/mmol-cat•h, 75 °C, 0.9 MPa ethylene pressure): some of the highest reported activities to date under practical industrial conditions (**23**).[99]

Tohi, Makio and Fujita revealed that, in conjunction with MAO, Zr complex **24** having two cumyl groups in the phenoxy-benzene ring forms uni-, bi-, and tri-modal PEs in a controlled manner simply by varying the polymerization temperatures.[100] Multimodal behavior in olefin polymerization often results from catalyst decay and/or non-stationary polymerization conditions such as mass transfer limitation and changes in chain transfer rates. However, they suggested based on experimental as well as theoretical studies that the multimodal behavior of complex **24** is most probably due to the fact that a bis(phenoxy–imine) complex can display more than one catalytically active species arising from the coordination modes of two non-symmetric ligands in an octahedral geometry. Similar multimodal behavior of fluorinated bis(phenoxy–imine) Ti complexes **14l–o** with MAO for the polymerization of propylene was reported by Saito and Fujita.[101] These results probably a unique strategy to produce well-defined multimodal polyolefins by a single homogeneous catalyst in a single stage polymerization process. The well-defined multimodal polymers are anticipated to possess an excellent combination of material properties and processability. Mitani and Fujita demonstrated that **25**/MAO copolymerizes ethylene and butadiene to afford copolymers with unique microstructures.[65]

As with the Ti complexes, on activation with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$, phenoxy–imine ligated Zr complexes show totally different catalytic behavior compared with that of MAO activation. For instance, Matsui, Saito and Fujita demonstrated that **25**/^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ generated ultra-high molecular weight (M_v 5050000) PE with 11 kg-PE/mmol-cat•h of activity while that with MAO afforded low molecular weight (M_v 10000) PE with 519 kg-PE/mmol-cat•h.[96] In addition, propylene polymerization with **25**/^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ produces isotactic-enriched PP (94 g-PP/mmol-cat•h, M_w 209000, *mm* 45.8%, T_m 103.5 °C) and with MAO an atactic oligomer (324 g-PP/mmol-cat•h).[88] It cannot be ruled out that the PP formed with complex **25** is an isotactic/atactic stereoblock PP produced through structural isomerization of an active species during propagation. The unusual difference turned out to be the result of the imine reduction by ^{i}Bu$_3$Al to produce amine and isobutene, which implies that the real active species of the ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ system is a bis(phenoxy–amine) complex with Al attached on the amine-nitrogen.

A specifically substituted bis(phenoxy–imine) Zr complex for ultra-high molecular weight polymers was developed by Ishii, Saito and Fujita.[102] They reported that complex **26** possessing a triethylsilyl, a 4-methoxyphenyl, and a methyl group in the ligand combined with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ at 70 °C forms exceptional molecular weight amorphous ethylene/propylene copolymer (propylene content: 20 mol %) with an M_w of 10200000 (vs PS standards). The molecular weight (M_w 10200000) represents the highest molecular weight known for linear, synthetic copolymers to date. Thus, phenoxy–imine ligated Zr complexes allow access to a wide range of materials from vinyl-terminated low molecular weight polymers to ultra-high molecular weight polymers by changing the ligand architecture and by the choice of cocatalyst.[103]

1.1.2.1.3. Hf Complexes. Bis(phenoxy–imine) Hf complexes have not been investigated as thoroughly as olefin polymerization catalysts when compared with the Ti- as well as the Zr- counterparts. Recently, however, some unique polymerization behavior of such complexes has been reported. Matsui and Fujita described that a Hf complex with a pair of phenoxy–imine chelate ligands combined with MAO exhibits very high ethylene polymerization activity comparable to that of Cp$_2$ZrCl$_2$ and generates moderate molecular weight PE (26 kg-PE/mmol-cat•h, M_v 17000, M_w/M_n 2.57); the activity and molecular weight values of **27** are just between those displayed by the corresponding Ti and Zr complexes.[29,65,104]

Saito and Fujita subsequently reported that Hf complex **27** combined with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ forms high molecular weight iPP (M_w 412000, mm 69.1%, T_m 123.8 °C).[88] Enantiomorphic site control accounts for the stereoselectivity. A site inversion may not occur in the catalyst system due to the steric congestion derived from the amine donor(^{i}Bu$_2$Al–N–Ph). This complex is the first isospecific system by site-control as a non-metallocene Hf-based catalyst system. With this result, phenoxy–imine ligated group 4 transition metal complexes are shown to produce PP architectures ranging from highly syndiotactic to isotactic via a chain-end- or a site-controlled mechanism by simple variations of central metal, ligand structure, and cocatalyst.[103]

A remarkable electron-withdrawing-substituent effect on catalytic properties was reported by Ishii and Fujita.[105] They described that Hf complex **28a** possessing a perfluorophenyl group attached to the imine-nitrogen produces higher molecular weight PEs with increased activities relative to the non-fluorinated Hf congener **27**. Moreover, the complex shows enhanced incorporation ability for propylene to form copolymers with higher propylene contents. The same substituent effect was also observed for the corresponding Zr complex **28b**.

1.1.2.2. V Complexes. Milani et al. studied ethylene/propylene copolymerization using V complexes **29**, **30** (Fig. 16) with various phenoxy–imine ligands.[106] They reported that these complexes with Et$_2$AlCl show similar catalytic properties (e.g., activity 1.8 kg-polymer/mmol-cat•h, propylene content 54 wt %, [η] 2.0) to commercial catalysts such as V(acac)$_3$.

Ethylene polymerization behavior of a V complex **31** with a pair of phenoxy–imine ligands was investigated by Matsui.[104] He showed that the cocatalyst employed has a profound influence on catalytic activity of **31**. With MAO or Et$_3$Al, **31** is a poor catalyst for ethylene polymerization. In contrast, employing Et$_2$AlCl or EtAlCl$_2$ as a cocatalyst affords enhanced activities and increased product molecular weights (Et$_2$AlCl; 2.1 kg-PE/mmol-cat•h, M_v 450000, EtAlCl$_2$ 4.1 kg-PE/mmol-cat•h, M_v 776000). Considering that V(Ⅳ) is readily reduced to V(Ⅱ) state, which is a common deactivation pathway

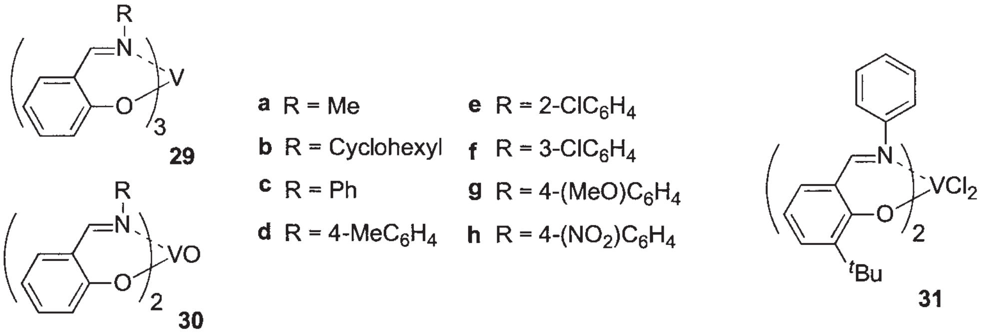


Fig. 16.

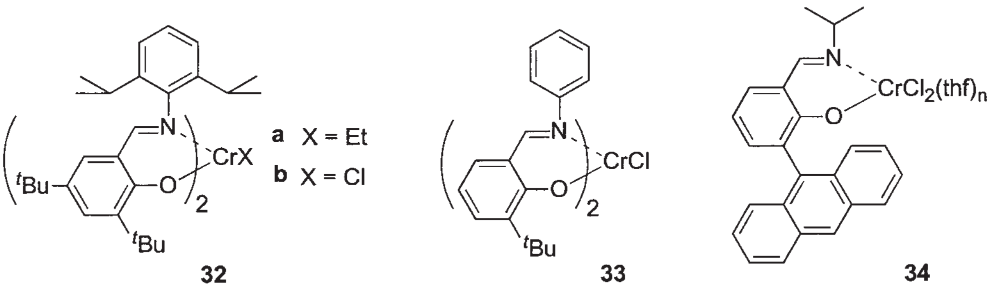


Fig. 17.

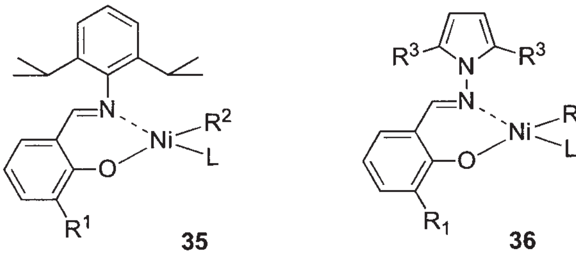


Fig. 18.

for V catalysts, one cannot conclude that the reducing ability of the cocatalyst is probably related to this observation.

Significantly, based on bis(phenoxy–imine) V complexes, Nakayama, Bando and Fujita developed highly-active, thermally robust new V-based catalyst systems.[107] The V catalyst system contains a bis(phenoxy–imine) V complex **30c** and a $MgCl_2$-based compound. Notably, the catalyst system exhibits enhanced activity with an increase in temperature (25 °C–75 °C) and has a very high activity of 65.1 kg-PE/mmol-cat•h at 75 °C with a steady uptake of ethylene (1 atm). These results are of great significance because V-based catalysts display low activities at elevated temperatures, mainly due to the thermal instability of the active species.

1.1.2.3. Cr Complexes. Gibson et al. investigated the structures and ethylene polymerization properties of Cr complexes **32** (Fig. 17) bearing phenoxy–imine ligands.[108] Ethyl complex **32a** adopts a distorted square pyramidal geometry with C_2 symmetry, whereas CH_3CN adduct possesses an octahedral structure with C_2 symmetry, if one ignores the nonequivalence of the chloride and CH_3CN ligands. These complexes combined with Et_2AlCl are active catalysts for the polymerization of ethylene (max. 96 g-PE/mmol-cat•h, 1.0 MPa ethylene pressure) and yield linear, high molecular weight PEs with broad molecular weight distributions (M_w ca. 2000000, M_w/M_n 3.6–19.9). Gibson et al. pointed out the possibility that an active species may possess only one phenoxy–imine ligand.

Ethylene polymerization properties of a Cr complex **33** having two phenoxy–imine ligands was also studied by Matsui.[104] He reported that, on activation with MAO, **33** can produce narrow molecular weight distribution PEs with high efficiency (Al/Cr 50, 590 g-PE/mmol-cat•h, M_w 70000, M_w/M_n 2.48). The activity, 590 g-PE/mmol-cat•h, is very high for a Cr complex with no Cp ligand under the given conditions. A Cr complex having one phenoxy–imine ligand is proposed to be a catalytically active species.

Recently, using in situ Cr complex synthesis and MAO activation, Jones and Gibson found a Cr complex with a phenoxy–imine ligand having a bulky *ortho*-phenoxy substituent and a small imine substituent (**34**), which affords a very high ethylene polymerization activity of 1.76 kg-PE/mmol-cat•h.[109]

1.1.2.4. Ni Complexes. Neutral Ni complexes for olefin polymerization have attracted considerable attention because they exhibit reduced interaction with the heteroatoms of functional monomers due to their reduced charge at the catalytic center. With such characteristics, these complexes are potentially viable catalysts for the copolymerization of olefins with polar monomers. Though P–O ligated Ni complexes (SHOP-type catalysts) are the most studied neutral Ni catalysts, a new class of neutral Ni complexes **35** (Fig. 18) bearing phenoxy–imine ligands have been developed by Grubbs et al.[110,111] and Ittel et al.[112]

Wang, Younkin and Grubbs reported that these Ni complexes with a phosphine scavenger such as $Ni(COD)_2$ or $B(C_6F_5)_3$ can be highly-active catalysts for the polymerization of ethylene.[110] Some of these complexes were described to display activities rivaling those of early metallocenes and Ni complexes with di-imine ligands developed by Brookhart et al. (max. 67.3 kg-PE/mmol-cat•h, 35 °C, 1.4 MPa ethylene pressure).[113] Complexes having sufficient steric bulk *ortho* to the phenoxy-oxygen are able to function as single-component catalysts. With these catalysts, moderate to high molecular weight PEs having ca. 10–50 branches per 1000 carbons are produced. An electron-withdrawing substituent *para* to the phenoxy-oxygen enhances catalytic activity. In addition, bulky substituents *ortho* to the phenoxy-oxygen increase catalytic activity and reduce the number of branches in the resultant PE.

These Ni catalysts are also capable of promoting homo- and copolymerization of styrene and norbornene and copolymerization of ethylene with higher α-olefins such as 1-hexene and 1-octene.[112] Ethylene polymerization ability of complexes **35** with BPh_3(i) or $B(C_6F_5)_3$ (ii, iii) was investigated by Johnson and Ittel (i: TON 787, ii: TON 8760, iii: TON 8300, r.t., 28–35 kPa). They also examined copolymerization ability of styrene and norbornene (i: TON 183, styrene content 8%; ii: TON 60, styrene content 7%) as well as ethylene/α-olefin polymerization activity in the presence of $B(C_6F_5)_3$ (ii: 1-hexene, 116.1 branches per 1000 carbons; 1-octene, 112.0 branches per 1000 carbons; iii: 1-octene, 178.7 branches per 1000 carbons, 28–35 kPa ethylene pressure).

A remarkable feature of these Ni complexes is that they show considerable tolerance toward functional groups, allowing ethylene polymerization in the presence of polar additives (e.g., acetone, ethanol, water, and triethylamine). Moreover, Grubbs et al. reported that these catalysts are capable of copolymerizing ethylene with functionalized norbornenes such as 5-norbornen-2-ol to produce cyclic olefin copolymers with hydroxy or ester functionality.[111] No information concerning the copolymerization of ethylene and polar monomers with the polar functionality directly attached to the C–C double bond (e.g., methyl acrylate, vinyl acetate) is reported. A number of theoretical studies on these phenoxy–imine ligated Ni complexes were reported by Michalak, Deubel, and Ziegler.[114–116]

Mackenzie and Killian described olefin polymerization behavior of phenoxy–imine ligated Ni as well as Zr complexes **36** having 2,5-disubstituted pyrroles on the imine-nitrogen.[117,118]

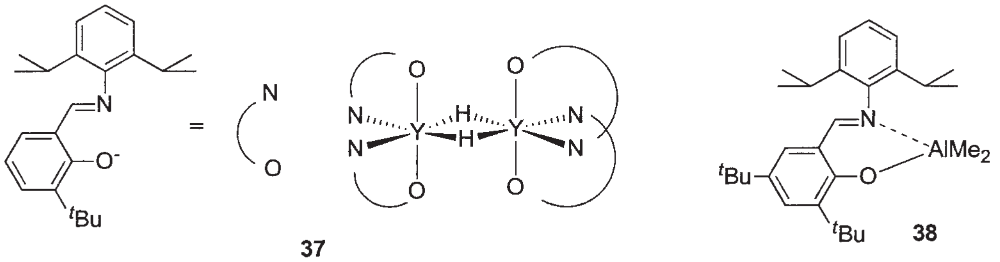
1.1.2.5. Other Metal Complexes. Emslie and Piers prepared Sc and Y complexes **37** (Fig. 19) containing phenoxy–imine ligands. μ-Hydride complex **37** exhibits no polymerization activity under 1 atm of ethylene at room temperature and very low activity under 4 atm.[119] This is probably because the complex reacts as a dimer rather than by an initial dissociative step to give a reactive monomer species, despite the high steric congestion associated with the bis(phenoxy–imine) ligand environment.

Nguyen and co-workers synthesized a number of Al complexes incorporating phenoxy–imine ligands of the type **38**. The molecular structures of some of the complexes were determined by X-ray diffraction. In the presence of appropriate Lewis acids such as $B(C_6F_5)_3$, these complexes are capable of converting ethylene to high molecular weight PEs.[120]

A series of Al complexes **39** (Fig. 20) bearing phenoxy–imine ligands and their corresponding cationic complexes **40** were synthesized and characterized by Cameron and Gibson.[121] Pappalardo and Pellecchia reported that activities of these complexes to form PEs were very low.[122]

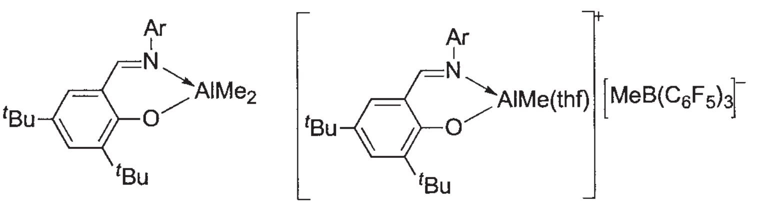
So far, readers have probably noted that phenoxy–imine ligands give highly-active catalysts with both early and late transition metals (e.g., Ti, Zr, Hf, V, Cr, Ni). This is unusual since normally a specific combination of a metal and a ligand provides a highly-active catalyst. Consequently, these results indicate the very high potential of phenoxy–imine donors as ligands for olefin polymerization catalysts.[30]

1.2. [O⁻, O] [O⁻, P] Phenoxy–Aldehyde/Ether/Phosphine. Matilainen et al. studied the structures and olefin polymerization properties of Ti and Zr complexes of the types **41** and **42** (Fig. 21).[123] These complexes are crystallographically characterized to have octahedral geometries with *cis*-located chlorides. In the presence of MAO, these complexes ex-



37 **38**

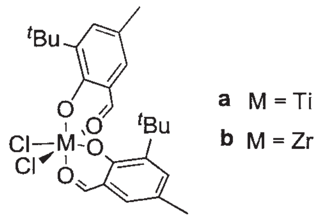
Fig. 19.



39 **40**

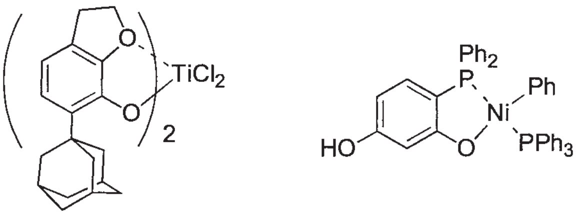
- **a** Ar = $2,6\text{-}Me_2C_6H_3$
- **b** Ar = $2,6\text{-}{}^iPr_2C_6H_3$
- **c** Ar = $3,5\text{-}(CF_3)_2C_6H_3$
- **d** Ar = $4\text{-}NO_2C_6H_4$
- **e** Ar = $4\text{-}ClC_6H_4$
- **f** Ar = 1-naphthyl
- **g** Ar = ${}^tBu$

Fig. 20.



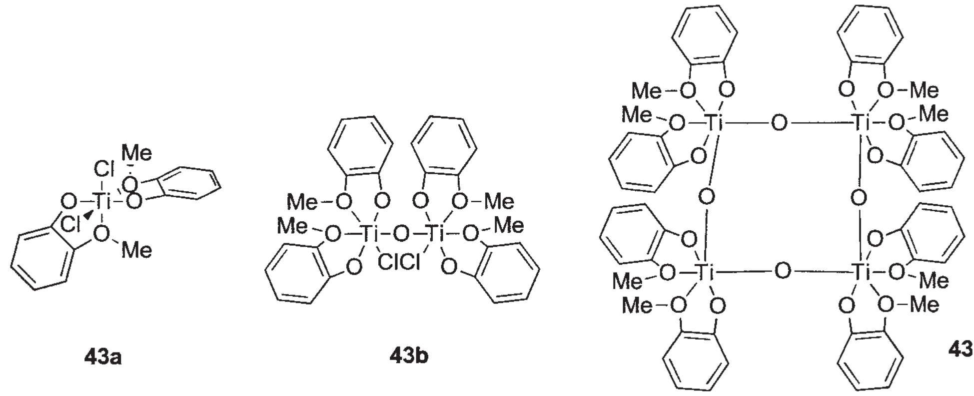
41 **42**

Fig. 21.



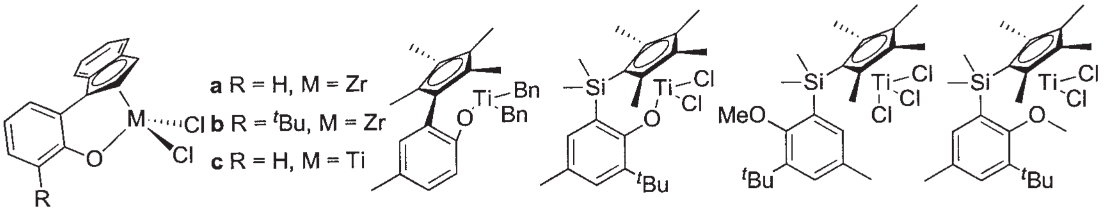
44 **45**

Fig. 23.



43a **43b** **43c**

Fig. 22.



46 **47** **48** **49** **50**

Fig. 24.

hibit very high activities in ethylene polymerization and high molecular weight PEs (**41a**: 3.83 kg-PE/mmol-cat•h, M_w 700000; **41b**: 1.40 kg-PE/mmol-cat•h, M_w 633000; **42**: 0.74 kg-PE/mmol-cat•h, M_w 906000). Interestingly, the PEs produced possess broad molecular weight distributions (**41a**: M_w/M_n, 16.0; **41b**: M_w/M_n, 17.1; **42**: M_w/M_n, 16.7), suggesting the presence of more than one catalytically active species in the polymerization. Complex **41a** also promotes ethylene/1-hexene copolymerization and affords extremely high molecular weight copolymers with broad molecular weight distribution (2.50 kg-polymer/mmol-cat•h, 1-hexene content: 3 mol %, M_w 1650000, M_w/M_n, 28.8).

Sobota and co-workers developed a new class of Ti complexes **43** (Fig. 22) containing phenoxy–ether (guaiacol) ligands for the polymerization of ethylene.[124] The molecular structure of **43a** reveals an octahedral geometry about the Ti center with a *trans*-phenoxy-O, *cis*-ether-O and *cis*-Cl disposition, indicative of the coordination of ether-oxygen to the Ti metal. Among the complexes examined, μ-oxo complex **43b** exhibits the highest activity of 27.8 kg-PE/mmol-Ti/h under 0.5 MPa of ethylene pressure in combination with $MgCl_2$/Et_3Al/Et_2AlCl. No molecular weight values were reported.

Highly-active phenoxy–ether ligated Ti complexes were reported by Suzuki, Inoue and Fujita.[125] They showed that a Ti complex **44** (Fig. 23) on activation with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ or MAO displays very high activities in ethylene polymerization (^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$: 3.48 kg-PE/mmol-cat•h, MAO: 2.812 kg-PE/mmol-cat•h). A bulky substituent *ortho* to the phenoxy-oxygen is required for the complex synthesis as well as the achievement of high activity.

Stazewski et al. described ethylene polymerization with phenoxy–phosphine ligated Ni complexes **45** formed in situ from catalyst precursor solutions.[126] The viscosity-average molecular weights (M_v) of the polymers range from 27000 to 1070000, depending on the ylide used. It should be pointed out that this catalyst system is active even in polar solvents such as ethyl acetate, acetone and *N*,*N*-dimethylformamide; moreover, no alkylaluminum compounds are needed for the polymerization.

2. Dianionic Ligands. 2.1. [O$^-$, Cp$^-$]. The high potential of group 4 transition metal complexes **46** (Fig. 24) incorporating bridged phenoxy–Cp ligands as olefin polymerization catalysts was first disclosed by Kawai and Fujita.[127,128] They reported, for example, that **46a** in the presence of MAO displays a very high ethylene polymerization activity (25 °C, 1.25 kg-PE/mmol-cat•h), suggesting that a bridged phenoxy–Cp donor can be a good ligand for group 4 metal catalysts.

Chen and Marks developed a Ti complex **47** having a phenoxy–Cp ligand capable of polymerizing various olefins with high efficiency.[129] On activation with $Ph_3CB(C_6F_5)_4$, this complex is a highly-active catalyst for the polymerization of ethylene, propylene and styrene and produces high molecular weight PE (activity 2.10 kg-PE/mmol-cat•h, M_w 1140000, T_m 142 °C), atactic PP (activity 3.82 kg-PP/mmol-cat•h, M_w 23600), and atactic PS (activity 43.3 kg-PS/mmol-cat•h, M_w 8000). The open nature of the catalytic site, similar to that of CGC, is probably responsible for the low degree of polymerization stereocontrol, resulting in the formation of atactic PP and PS.

A new series of Ti complexes featuring phenoxy–Cp chelate ligands (**48**) were introduced by Imai and Miyatake; these are highly useful catalysts for the polymerization of various olefins.[130,131] One of the key features of these catalysts is the open nature of the catalyst active site that allows them to incorporate sterically large monomers into a growing polymer chain. Moreover, these catalysts are capable of producing high-molecular-weight polymers at high temperatures with very high productivity. Consequently, these remarkable catalysts can be utilized in high-pressure anionic polymerization processes. When activated with $^i Bu_3Al/[PhNHMe_2][B(C_6F_5)_4]$, complex **48** exhibits outstandingly high activity at a very high temperature of 180 °C in ethylene/1-hexene copolymerization (4400 kg-polymer/mmol-cat•h, 2.5 MPa ethylene pressure, 1-hexene content 7.1 mol %). Notably, these Ti complexes catalyze the copolymerization of propylene and 1-butene with significantly high productivity and produce high molecular weight amorphous copolymers which possess numerous superior material properties to those of existing propylene/1-butene copolymers. These complexes were also reported to mediate the copolymerization of ethylene and 3-methylbutadiene via predominant 1,4-insertion of 3-methylbutadiene and to give substantially linear copolymers. These copolymers can be used as materials for synthetic rubbers and thermoplastic elastomers.

Nabika and Miyatake also reported the catalytic performance of the related complexes of the types **49** and **50** (Ti complexes with Cp–ether ligands).[132] It was shown that the trivalent Ti complex **50** has an advantage over the tetravalent Ti complex **49** in ethylene/1-hexene copolymerization (14.9 kg-polymer/mmol-cat•h, 0.6 MPa ethylene pressure), butadiene polymerization (40 g-polymer/mmol-cat•h), and ethylene/5-hexen-1-ol copolymerization (118 g-polymer/mmol-cat•h, 0.6 MPa ethylene pressure, 5-hexen-1-ol content 0.68 mol %) in the presence of $^i Bu_3Al/Ph_3CB(C_6F_5)_4$ cocatalyst. The coordination chemistry of bridged phenoxy–Cp or alkoxy–Cp ligands has been described by Siemeling in a recent review.[133]

2.2. [O$^-$, O$^-$] Bisphenoxy [O$^-$, N$^-$] Phenoxy–Amide. Ti and Zr complexes bearing various sterically hindered bis(phenoxy) or bis(naphthoxy) ligands for olefin polymerization were reported by van der Linden and Schaverien (Fig. 25).[134] In the presence of MAO, these complexes are capable of converting ethylene to PEs that typically possess broad molecular weight distributions (M_w/M_n 10.5–24), implying the presence of more than one active species. Remarkably, **51a** and **51b** polymerize 1-hexene in an isotactic fashion and form regioregular isotactic poly-1-hexene with very high molecular weight (M_w 674000, M_w/M_n 2.23). They also reported that, on activation with MAO, **51a** and **51b** are active towards butadiene and produce polybutadiene with predominant 1,4-insertion.

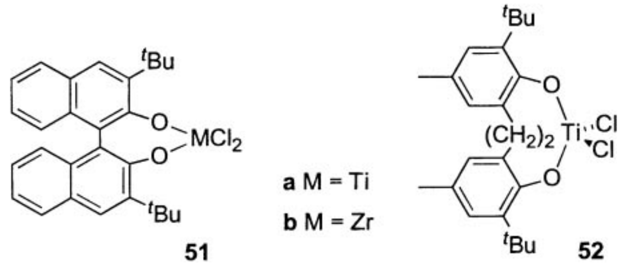


Fig. 25.

The structural properties and ethylene/styrene copolymerization behavior of Ti complexes **52** containing ethylene-bridged bis(phenoxy) ligands were investigated by Fokken and Okuda.[135] These complexes are demonstrated to possess tetrahedrally coordinated Ti metal centers and C_2 symmetry by single-crystal X-ray structural analyses. NMR studies revealed a fluxional process that can be described as a ring inversion ($\Delta G^\#$ ca. 60 kJ/mol). In the presence of MAO, these complexes efficiently copolymerize ethylene and styrene with remarkably high incorporation of styrene (e.g., activity 1 g-polymer/mmol-cat•h, styrene content 36.4 mol %) compared with the related Ti complexes having methylene- or sulfur-bridged ligands. The high incorporation ability for styrene is probably the result of the open coordination sphere around the Ti center. No homopolymerization data were reported. Computational studies of the bis(phenoxy)-based catalysts were performed by Froese and Morokuma.[136,137]

Takaoki et al. disclosed the catalytic properties of Ti complexes having phenoxy–amide ligands (Fig. 26) for the polymerization of ethylene and α-olefins (**53**: activity 1.05 kg-PE/mmol-cat•h, 60 °C, 0.4 MPa, $^i Bu_3Al/Ph_3CB(C_6F_5)_4$ cocatalyst).[138]

A new Cr complex bearing tris[bis(naphthoxy)] ligands **54** was reported recently by Ikeda and Yasuda.[139] In the presence of MMAO or Et_2AlCl, **54** polymerizes ethylene to give broad molecular weight distribution PEs with low activities (max. 15 g-PE/mmol-cat•h, M_w 1200000, M_w/M_n 107), whereas a het-

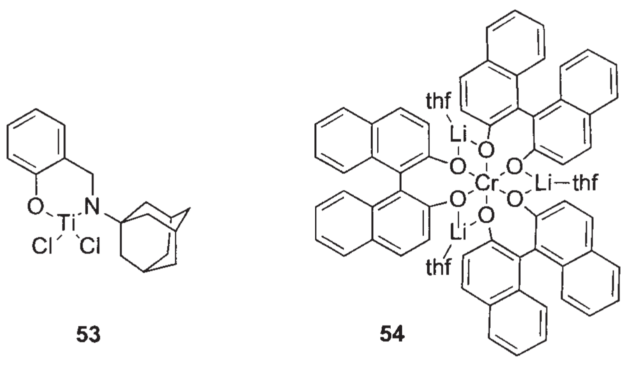
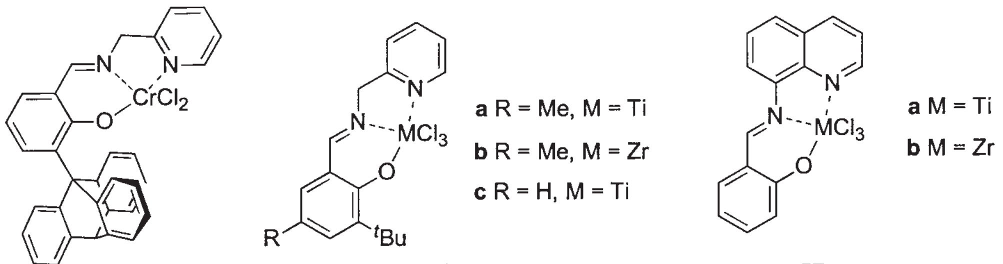


Fig. 26.



55 **56** **57**

Fig. 27.

erogeneous catalyst using SiO_2 as a support exhibits higher activity (26 g-PE/mmol-cat•h).

C. Tridentate Ligands. Metal complexes incorporating tridentate phenoxy-based ligands, in particular those with $[O^-, O^-]$ based dianionic tridentate ligands, have been investigated intensively since the 1980s as promising olefin polymerization catalysts. Some of these complexes have been shown to display unique catalytic properties for the polymerizations of propylene, ethylene/styrene or dienes and to produce (co)polymers with distinctive microstructures.

1. Monoanioic Ligands. 1.1. $[O^-$, N, N] Phenoxy–Imine–Pyridine. With combinatorial methods, Jones and Gibson discovered a Cr complex **55** (Fig. 27) containing a phenoxy–imine–pyridine chelate ligand that compares favorably with the most active homogeneous Cr-based olefin polymerization catalysts.[109] Complex **55** combined with MAO has a very high activity (6.97 kg-PE/mmol-cat•h, 50 °C, 0.4 MPa ethylene pressure) and forms low molecular weight PE (M_w 1100, M_w/M_n 2.1). These results clearly demonstrate that a combinatorial approach is applicable to the discovery of new olefin polymerization catalysts composed of phenoxy–imine-based ligands and transition metal centers.

Ittel et al. developed group 4 transition metal complexes with tridentate phenoxy–imine–pyridine ligands **56a**, **56b** and **57**.[140] These complexes are highly-active catalysts for ethylene polymerization when activated with MMAO (**56a**: 0.68 kg-PE/mmol-cat, **57a**: 0.40 kg-PE/mmol-cat, 3.45 MPa ethylene pressure).

Very high activities for ethylene homopolymerization as well as ethylene/propylene copolymerization were also reported by Takagi and Fujita for Ti complexes **56c** bearing phenoxy–imine–pyridine ligands.[141] The highest activity is obtained with complex **56c** using $^iBu_3Al/Ph_3CB(C_6F_5)_4$ as a cocatalyst (ethylene polymerization 4.71 kg-PE/mmol-cat•h, 75 °C; ethylene/propylene copolymerization 2.32 kg-polymer/mmol-cat•h, 25 °C, propylene content 12.3 mol %).

Cameron and Gibson studied the structures and ethylene polymerization behavior of Al complexes with phenoxy–imine based tridentate ligands (Fig. 28).[142] The additional ligand Ls were introduced to mitigate the high reactivity of the corresponding cationic complex, which may abstract an aryl group from an arylborate anion without an additional donor. Complexes **58a** and **58c** were crystallographically characterized to have distorted trigonal bipyramidal geometries. A cation complex derived from complex **58a** and $B(C_6F_5)_3$ was also characterized by ^1H NMR and shown to exist as a fully separated ion pair. Upon activation with $B(C_6F_5)_3$, complexes **58a** and **58b** exhibit low activity (50 and 110 g-PE/mmol-cat•h, respectively, 0.5 MPa ethylene pressure) and generate high molecular weight PEs (M_w 172000 and 218000, respectively), while complexes **58c** and **58d** are inactive. The observations are attributable to the electron-donating nature of Ls, as evidenced by the Al–L bond distances.

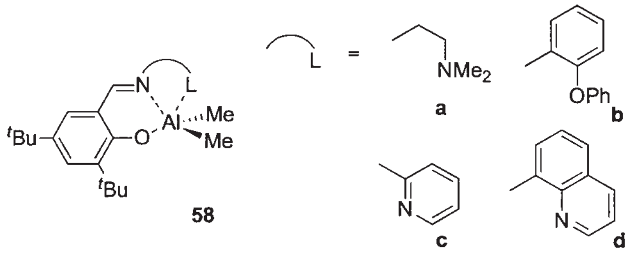


Fig. 28.

2. Dianionic Ligands. 2.1. $[O^-$, S, $O^-]$, $[O^-$, Te, $O^-]$. Miyatake and Kakugo pioneered the field of bis(phenoxy)-based olefin polymerization catalysts, and discovered a new family of Ti complexes **59** (Fig. 29) containing tridentate bis(phenoxy)–thioether ligands.[143a] Upon activation with MAO, **59a** shows similar activity in the polymerization of ethylene to Cp_2ZrCl_2 for short time polymerization and produces higher molecular weight polymer (**59a** 10.9 g-PE/mmol-cat/s, 20 °C, 10 seconds, M_w 3600000, M_w/M_n 2.0; Cp_2ZrCl_2 12.7 g-PE/mmol-cat/s, M_w 620000, M_w/M_n 2.0). Also, **59a** polymerizes propylene with much higher activity than Cp_2ZrCl_2 in liquid monomer and forms ultra-high molecular weight PP (1 h: 8.9 kg-PP/mmol-cat•h, 20 °C, $M_w > 8000000$, M_w/M_n 2.2; Cp_2ZrCl_2 1.6 kg-PP/mmol-cat•h, M_w 76000, M_w/M_n 2.0). The molecular weight value ($M_w > 8000000$) represents one of the highest molecular weights among PPs ever reported. The high molecular weight PP obtained is atactic and contains a high proportion of regioirregular units.

Alternatively, **59a** with MAO is capable of catalyzing the polymerization of styrene and generates highly syndiotactic (>98%) PS with activities of up to 2.35 kg-PS/mmol-cat•h (80 °C, M_w 87000, M_w/M_n 2.1). Interestingly, copolymerization of ethylene with styrene using **59a**/MAO yields highly alternating copolymers with isotactic styrene units. In addition, **59b** (O^iPr)/MAO can polymerize various conjugated and non-conjugated dienes. For example, **59b** converts butadiene to polybutadiene having a predominantly *cis*-1,4-structure (98%), whereas **59b** polymerizes 1,5-hexadiene to afford poly(1,5-hexadiene) having unique microstructure. Therefore, the development of Ti complexes with bis(phenoxy–imine)–

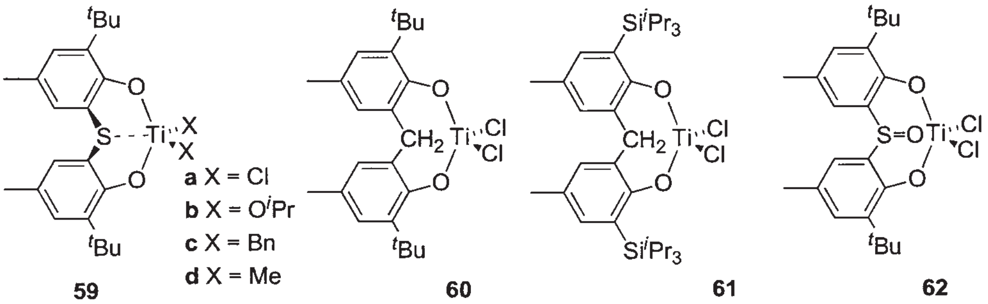


Fig. 29.

thioether ligands has opened a number of opportunities for the synthesis of unique polymers. Porri et al. showed by X-ray analysis that complex **59b** exists as a dimer and that the coordination environment about each Ti center is best described as a distorted octahedron.[144] In addition, they revealed a significant S–Ti interaction (distance 2.724(2) Å), which probably accounts for higher activities compared to that of complex **60** where the S atom is replaced by a methylene bridge in the bis(phenoxy) ligand.

Computational studies on Ti complexes with bis(phenoxy)–thioether ligands performed by Froese and Morokuma indicated that low ethylene insertion barriers and thus high activities are expected as a consequence of the coordination of S atom to the Ti center during catalysis.[136,137]

Takaoki and Miyatake recently reported a Ti complex with a bis(phenoxy)–thioether having sterically more demanding ^{i}Pr$_3$Si groups instead of the ^{t}Bu groups in the positions *ortho* to the phenoxy-oxygens (**61**).[145] This complex with both MAO and ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ activation displays higher ethylene polymerization activities and forms higher molecular weight polymers (e.g., MAO activation, 1.05 kg-PE/mmol-cat•h, 60 °C, 0.4 MPa, M_w 710000) compared to **59**.

After Kakugo's initial report, the catalytic behavior of **59** and its dibenzyl derivative for the polymerization of ethylene, 1-hexene and butadiene was described by van der Linden and Schaverien.[134] These complexes in conjunction with MAO afford broad molecular weight distribution PEs with high productivity (**59a**: 4.74 kg-PE/mmol-cat•h, M_w 350000, M_w/M_n 11.9, **59c**: 0.50 kg-PE/mmol-cat•h, M_w 340000, M_w/M_n 7.0, 20 °C, 0.3 MPa ethylene pressure). In addition, these complexes with MAO convert 1-hexene to regioregular atactic poly(1-hexene)s with moderate molecular weights (**59a**: M_w 7800, M_w/M_n 1.78; **59c**: M_w 19000, M_w/M_n 1.71). **59c**/MAO is also active for the polymerization of butadiene to produce polybutadiene (52.8 g-polymer/mmol-cat•h, 1,2-vinyl: 15%, 1,4-*trans*: 20%, 1,4-*cis*: 65%). Fokken and Okuda reported the synthesis of complex **59d**, which polymerizes ethylene when activated with B(C$_6$F$_5$)$_3$, albeit in low yield.[143b]

Sernetz and Mülhaupt presented a study using Ti complexes with various bis(phenoxy) ligands as olefin polymerization catalysts.[146] They revealed that Ti complexes having bis(phenoxy)–thioether (**59**) or bis(phenoxy)–sulfoxide (**62**) ligands show far higher activities towards ethylene/styrene copolymerization but display much lower incorporation ability for styrene than the corresponding ethylene-bridged complex. The methylene-bridged congener (**60**) provides a mixture of PE and PS with low activity, behavior similar to that of the Ti complex with hindered phenoxy ligand described by Seppälä et al. Based on analyses of the ethylene/styrene copolymers produced, they concluded that the bis(phenoxy)-based catalysts developed by Kakugo et al. are multisited catalysts similar to heterogeneous Ziegler–Natta catalysts.

The structures and ethylene polymerization properties of a series of Ti complexes **63** (Fig. 30) having Te-bridged bis(phenoxy) ligands were reported by Nakayama and Nakamura.[147] X-ray studies show that these complexes possess dimeric structures, and that the Te atom coordinates to the Ti center and thus the Te-bridged bis(phenoxy) ligand functions as a tridentate ligand. In the presence of MAO, these complexes have activities between those displayed by the corresponding methylene-bridged complex **60** and the sulfur-bridged complex **59** (70 g-PE/mmol-cat•h, M_w 15000, M_w/M_n 3.2). They also mentioned the structure and ethylene polymerization behavior of Ti complexes bearing both the Te-bridged bis(phenoxy) ligand and a Cp ligand (**64**: 130 g-PE/mmol-cat•h, M_w 67000, M_w/M_n 3.9).

Recently, Takaoki and Miyatake reported a V complex incorporating the bis(phenoxy)–thioether ligand (**65**) that polymerizes propylene in liquid monomer with moderate activity and provides a mixture of isotactic and atatic PP (420 g-PP/

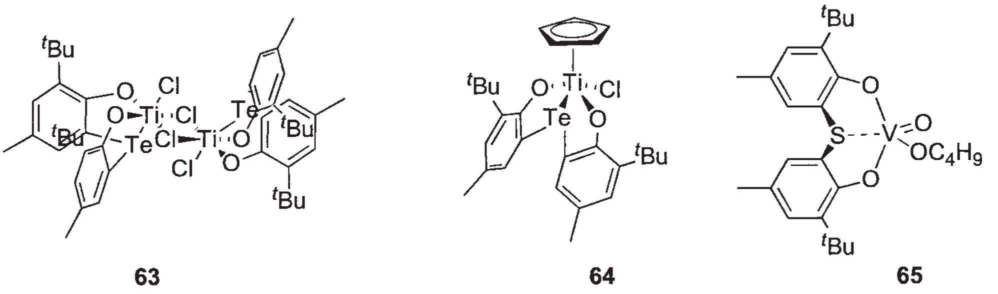


Fig. 30.

mmol-cat•h, 20 °C).[145] The mixture PP contains 68% *mm* triad and displays a T_m of 138 °C. The T_m is very high for an iPP produced by a V-based catalyst and is comparable to that formed with rac-$[C_2H_4\text{-(1-indenyl)}_2]ZrCl_2$/MAO catalyst system. An enantiomorphic site control mechanism is shown to be responsible for the observed stereo control.

2.2. [O⁻, N, O⁻] Bis(Phenoxy)–Imine/Pyridine. Chan et al. studied THF-bound Ti and Zr complexes **66** (Fig. 31) having bis(phenoxy)–pyridine ligands.[148] Ti complexes **66a** with MAO were shown to be poor catalysts for ethylene polymerization (max. 4.4 g-PE/mmol-cat•h). However, Zr complex **66b** shows a very high activity of 7.03 kg-PE/mmol-cat•h at 25 °C under atmospheric pressure, an activity which exceeds that seen with Cp_2TiCl_2/MAO system under identical conditions. The very high activity displayed by **66b** is intriguing, given the presence of the THF ligand that normally suppresses catalytic efficiency. Rigidly-organized ligand framework as well as pyridine coordination to the metal may be responsible for the observed high activity. Although the polymerization process is totally inhibited upon addition of THF, the possibility cannot be ruled out that the THF ligand functions as a fourth donor during catalysis.

Ittel et al. developed transition metal complexes with tridentate phenoxy–imine–phenoxy ligands (**67**),[149] which are highly-active catalysts for ethylene polymerization as well as ethylene/1-hexene copolymerization when activated with MAO. Among them, the complexes which possess bis(*tert*-butyl) groups exhibit relatively high activity, especially when the center metal is Ti or Zr (**67a** 64.4 g-PE/mmol-cat•h; **67b** 44.1 g-PE/mmol-cat•h, 25 °C, 6.9 MPa ethylene pressure: ethylene/1-hexene copolymerization, **67a** 492.4 g-polymer/mmol (18 h), 22.39 branches per 1000 carbons; **67b** 248.6 g-polymer/mmol (18 h), 21.0 branches per 1000 carbons, 1.4 MPa ethylene pressure).

Huang and Qian prepared a Ti complex with a bis(phenoxy)–imine and a Cp ligand (**68**) for olefin polymerization. Upon treatment with MAO, the complex is reported to show higher ethylene polymerization activity (15.6 g-PE/mmol-cat•h) and to form higher molecular weight (M_w 1630000) PE than Cp_2TiCl_2 (activity, 12.2 g-PE/mmol-cat•h, M_w 520000), though it displays a broad molecular weight distribution value (M_w/M_n 4.9).[69]

Group 4 transition metal complexes with tridentate bis(phenoxy)–amine ligands developed by Kol et al. are included in D.1.2.

D. Tetradentate Ligands. Until recently, only a few reports on the use of tetradentate phenoxy-based ligands have appeared. However, during the past three years it has emerged that group 4 transition metal complexes having such ligands are viable catalysts for olefin polymerization. One of the key features of these complexes is their potentially rigidly-organized frameworks, which might result in thermally robust and/or highly stereoselective catalysts. In fact, incorporation of tetradentate phenoxy-based ligands into group 4 transition metals has given rise to unique catalysis (e.g., high activity at high temperature, living polymerization, and stereoselective polymerization).

1. Dianionic Ligands. 1.1. [O⁻, N, O⁻, N] Salen-Type and Bridged Phenoxy–Imine. Repo and Hakala studied ethylene polymerization behavior of a salen-type Zr complex (Fig. 32).[150] They found that a heterogeneous catalyst using SiO_2 as a support (complex **69**/SiO_2) on activation with MAO demonstrated much higher activities (max. 3.35 kg-PE/mmol-cat•h) than the corresponding homogeneous catalyst, **69**/MAO (120 g-PE/mmol-cat•h). This observation is highly unusual since the supported catalysts normally show lower activities than those of unsupported analogues.

Catalytic behavior of a series of polymethylene-bridged bis(phenoxy–imine) Zr complexes **70** for ethylene polymerization was investigated by Ishii and Fujita. They found that activities exhibited by the complexes in combination with MAO increased as the number of methylene units $[-(CH_2)-_n$:

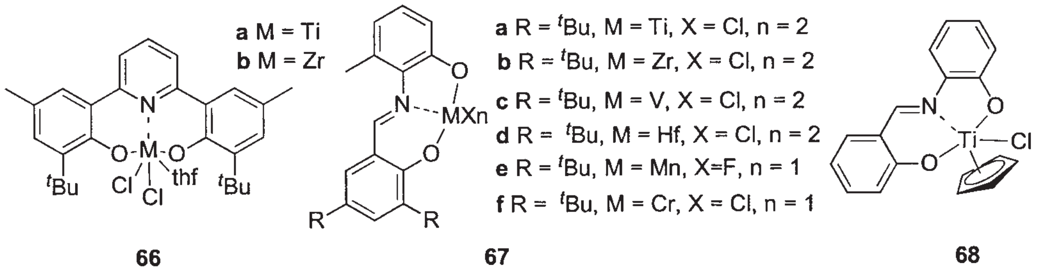


Fig. 31.

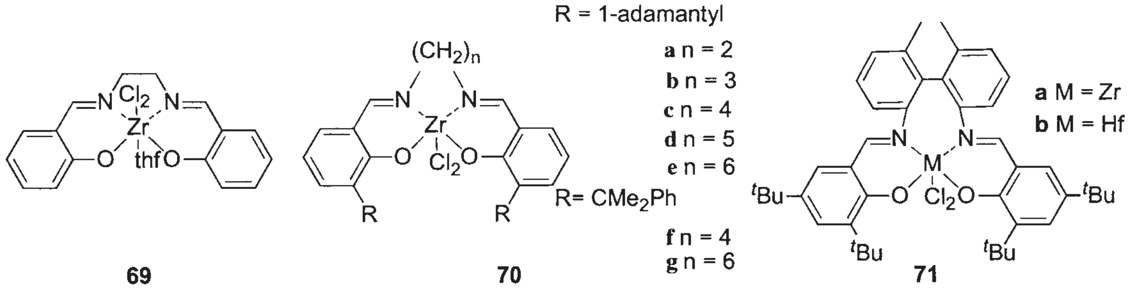


Fig. 32.

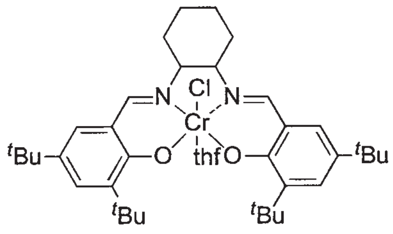
$n = 2$–6] increased (max. **70g**, 103.8 kg-PE/mmol-cat•h, 75 °C).[151] Considering that chlorine-bound sites are potential polymerization sites and thus a complex with a pair of *cis*-located chlorine-bound sites can be an efficient catalyst, one can conclude that the observed activity increase is probably associated with the increase in the number of isomers with *cis*-located chlorine-bound sites; this conclusion was supported by theoretical studies. Notably, hexamethylene bridged complex **70g** is a thermally robust catalyst and displayed a very high activity of 143 kg-PE/mmol-cat•h under commercially relevant solution polymerization conditions (150 °C, 3.0 MPa ethylene pressure); this is viewed as promising from a commercial perspective.

Woodman and Scott developed a unique strategy for the stereochemical control of a resulting complex and synthesized rigidly-organized biaryl-bridged bis(phenoxy–imine) Zr, and Hf dichloride complexes (**71**) in which two chlorine atoms are forced to occupy *cis*-positions, suggesting the high potential of these complexes for olefin polymerization.[152] The corresponding alkyl complexes are prone to decomposition via rapid alkyl transfer to the imine-carbon in the complex. This unfavorable reaction is probably a result of the conjugated nature of the ligand, because such reactions are not observed for non-bridged or bridged non-conjugated ligand systems, with the exception of ligands having highly electron-withdrawing substituents such as a perfluorophenyl group. Knight and Scott demonstrated a ligand modification that can sterically block the alkyl transfer, leading to a long-lived catalyst for ethylene polymerization, though with low activity (65 g-PE/mmol-cat•h).[153] O'Shaughnessy and Scott have extended the strategy to biarylamido complexes.[154]

Fujimoto et al. disclosed that Cr complexes having bridged bis(phenoxy–imine) ligands **72** (Fig. 33) combined with $EtAlCl_2$ can be catalysts for the polymerization of ethylene and norbornene, though with low activities (e.g., ethylene polymerization, 68 g-PE/mmol-cat•h, r.t.).[155]

The ability of a salen-type Mn complex to polymerize ethylene or propylene was recently reported by Ban and Murata.[156] Complex **73** is capable of polymerizing ethylene, though it shows low activity when activated with MAO (0.1 g-PE/mmol-cat•h, r.t.). However, when supported on $MgCl_2$ and activated with Et_2AlCl, the complex exhibited higher activity (25 g-PE/mmol-cat•h, r.t.). The supported catalyst produced highly isotactic polypropylene (0.7 g-PP/mmol-cat•h, r.t., *mmmm* 80.3%).

1.2. [O$^-$, N, O$^-$, {N, O, S}] Bis(Phenoxy–Amine) with an Additional Heteroatom. Kol and Goldschmidt developed a new series of significant catalysts for the polymerization of 1-hexene.[157–163] They studied the structures and 1-hexene polymerization behavior of C_s-symmetric group 4 transition metal complexes with bis(phenoxy)–amine ligands bearing extra donors (i.e., amine, ether, pyridine, thioether) (**74**, **75**, Fig. 34) and revealed the effects of additional pendant donors on catalytic performance.[161] Single-crystal X-ray analyses indicated that these complexes adopt a distorted octahedral structure with a *trans*-O, *cis*-N/extra donor, and *cis*-benzyl ligand arrangement. In combination with $B(C_6F_5)_3$, the activity order of the Zr complexes **74** in terms of extra donors is OMe > NMe_2 > SMe, whereas that of the Hf complexes is SMe > OMe > NMe_2. The Hf complex **75d** bearing the extra S donor displays the highest activity reported to date for Hf-based 1-hexene polymerization catalysts (35 kg-polymer/mmol-cat•h). Interestingly, Kol and Goldschmidt described that for Zr complexes with extra NMe_2 donors, the steric bulk in the position *ortho* to the phenoxy-oxygen has little influence on catalytic activity (though detailed activity values were not given). Among the complexes examined, **74b** (Zr, donor OMe) with $B(C_6F_5)_3$ demonstrates the highest activity in 1-hexene polymerization and provides poly-1-hexene with high molecular weight (50 kg-polymer/mmol-cat•h, M_w 80000, M_w/M_n 3.0, neat 1-hexene, r.t.). In contrast, a Zr complex with a tridentate ligand having identical bis(phenoxy)–amine moiety but lacking the extra amine donor group on the side arm is a poor catalyst for 1-hexene polymerization (23 g-



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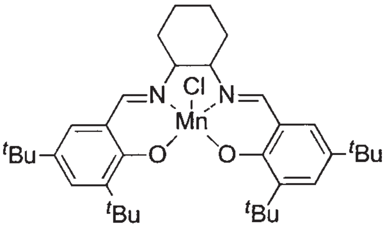
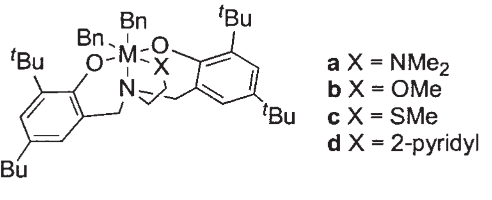
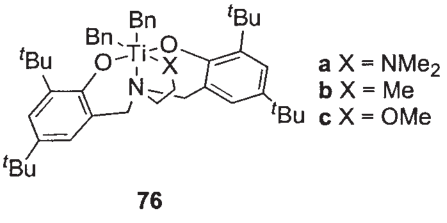


73

Fig. 33.



74 (M = Zr), **75** (M = Hf)



76

Fig. 34.

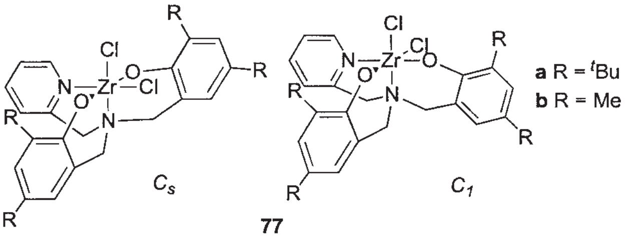
oligomer/mmol-cat•h), indicating the dramatic effect of the extra amine donor on the enhancement of catalytic activity.

The effect of the extra amine donor on the catalytic performance of the Ti congener **76a** is rather different from that observed for the Zr complex **74a**.[162] Thus, **76b** having no extra donor displays somewhat higher activity than **76a** with the extra donor and produces lower molecular weight poly-1-hexene (M_w 1500, M_w/M_n ca. 2). However, **76a** catalyzes the living polymerization of 1-hexene and affords atactic monodisperse poly-1-hexene (M_w 14000, M_w/M_n 1.18). Therefore, in this case the extra amine donor curtails chain transfer reactions.

Making use of this remarkable extra donor effect, Tshuva, Kol and Goldschmidt realized highly-controlled living polymerization of 1-hexene.[163] Upon activation with $B(C_6F_5)_3$, Ti complex **76c** with the bis(phenoxy)–amine ligand having an extra ether donor polymerizes 1-hexene in a living fashion at room temperature and produces very high molecular weight monodisperse poly-1-hexene (M_w 445000, M_w/M_n 1.12). Notably, at 65 °C the catalyst system provides poly-1-hexene having fairly narrow molecular weight distribution (M_w 22000, M_w/M_n 1.30). This living polymerization was applied to the synthesis of a block copolymer poly(1-hexene-*b*-1-octene) (M_n 11600, M_w/M_n 1.2: poly-1-hexene segment, M_n 9000, M_w/M_n 1.2) at room temperature by sequential addition of the corresponding monomers.

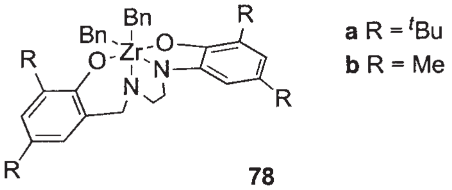
Toupance and Mountford thoroughly investigated the structures and solution dynamics of Zr complexes **77** (Fig. 35) with the bis(phenoxy)–amine ligand framework bearing an extra pyridine donor, using X-ray as well as variable-temperature NMR studies.[164] They revealed that these complexes have a tendency to exist as isomeric mixtures (e.g., C_1 and C_s symmetry isomers) in solution. These complexes are shown to be unreactive toward ethylene when activated with either MAO or $B(C_6F_5)_3$, though 1-hexene polymerization using one of the complexes is reported by Kol et al.[161]

1.3. [O⁻, N, O⁻, N] Bridged Phenoxy–Amine. Tshuva and Kol reported a C_2-symmetric Zr complex **78a** (Fig. 36) with a tetradentate bis(phenoxy–amine) ligand that forms highly isotactic poly(1-hexene) (>95%) in a living fashion at room temperature when activated by $B(C_6F_5)_3$ (activity, 18 g-polymer/mmol-cat•h, M_w 12000, M_w/M_n 1.15, neat 1-hexene).[165] This catalyst system is the first example of C_2-symmetrical system with no Cp ligand that is active in isospecific and living polymerization of higher α-olefins. The steric bulk of the *ortho*-phenoxy substituent seems to play a key role in achieving both living and isospecific polymerization since the similar complex **78b** having a methyl group in place of the *tert*-butyl group in the phenoxy-benzene ring produces atactic poly-1-hexene having a broadened molecular weight distribution (35 g-polymer/mmol-cat•h, M_n 23000, M_w/M_n 1.57). Although mechanistic details are not given, the C_2-symmetric catalyst environment should produce isotactic polymers.



77

Fig. 35.



78

Fig. 36.

Ronca and Busico studied propylene polymerization behavior of the Zr complexes **78a** and **78b** with bis(phenoxy–amine) ligands introduced by Kol et al.[166] They reported that **78a** on activation with $^iBu_3Al/PhNHMe_2B(C_6F_5)_4$ forms iPP (*mmmm* 80%, 25 °C) via a site-control mechanism, whereas **78b** produces slightly sPP (*r* 65%, 25 °C) via a chain-end control mechanism: in both cases polymerizations proceed in a non-living fashion and propylene insertions occur with highly selective 1,2-regiochemistry. They pointed out that these catalyst systems are good models for heterogeneous Ziegler–Natta active species. It is worth noting that propylene insertions into the structurally relevant bis(phenoxy–imine) Ti complexes **14h** occur with predominant 2,1-regiochemistry.[66,75] Theoretical calculations were performed on the regiochemistry of both bis(phenoxy–amine) Zr complexes and bis(phenoxy–imine) Ti complexes by Talarico, Busico and Cavallo.[85]

II. Summary

As introduced, a large number of phenoxy-based new olefin polymerization catalysts have been developed in both academic and industrial laboratories. It should be noted that phenoxy-based ligands generally provide higher activity catalysts with transition metals than other anionic-donor-based ligands (e.g., alkoxy, amido). DFT calculations performed on a group 4 metallocene catalyst imply that electronically flexible ligands have high potential for producing highly-active catalysts.[30] The reasons for the superior capabilities of phenoxy-based ligands have not yet been fully elucidated. However, the observed high activities may result from the electronically flexible nature of phenoxy donors, corroborating our concept regarding the development of highly-active olefin polymerization catalysts.[30]

All catalysts described herein are categorized according to the central metal and the associated ligand (Table 1). The phenoxy-based catalysts in Table 1 can access numerous polyolefinic materials with a wide variety of microstructures. A summary of the polyolefinic materials formed from these catalysts is given in Table 2. It can be seen from Table 2 that the catalysts have created a number of unique polymers that are difficult or impossible to synthesize with conventional catalysts. These achievements with respect to polymer syntheses depend on both the recent advances in rational catalyst design with the aid of computational science and the wide range of catalyst design possibilities of phenoxy-based catalysts. The wide possibilities originate from the easily varied steric

Table 1. Catalysts Categorized According to the Metal and Associated Ligand

Group	3	4			5	6	7	10	13
		Ti	Zr	Hf	V, Ta	Cr	Mn	Ni	Al
$[O^-]$		**1**, **2**, **3**	**4**		**5**, **6**				
$[O^-, N]$	**37**	**9**, **10**, **14**, **15**, **16**, **17**, **19**	**7**, **8**, **15**, **19**, **20**, **21**, **22**, **23**, **24**, **25**, **26**, **28**	**7**, **8**, **27**, **28**	**11**, **29**, **30**, **31**	**12**, **32**, **33**, **34**		**13**, **35**, **36**	**38**, **39**, **40**
$[O^-, O]$		**41**, **43**, **44**	**41**, **42**						
$[O^-, P]$								**45**	
$[O^-, Cp^-]$		**46**, **47**, **48**, (**49**, **50**)	**46**						
$[O^-, O^-]$		**51**, **52**, **54**	**51**						
$[O^-, N^-]$		**53**							
$[O^-, N, N]$		**56**, **57**	**56**, **57**			**55**			**58**
$[O^-, E, O^-]$ $E = S, Te$		**59**, **60**, **61**, **62**, **63**, **64**			**65**				
$[O^-, N, O^-]$		**66**, **67**, **68**, **76**	**66**, **67**						
$[O^-, N, O^-, N]$		**71**, **76**	**69**, **70**, **71**, **74**, **77**, **78**	**75**		**72**	**73**		
$[O^-, N, O^-, E]$ $E = S, O$		**76**	**74**, **77**	**75**					

and electronic properties of the phenoxy-based ligands, which are an important feature of the phenoxy-based catalyst systems.

It should be noted that most of the unique polymers in Table 2 have been reported over the past three years (2000–2002), during which the recently-developed phenoxy–imine based catalysts have made a significant contribution.[30,73,74,103] Thus, phenoxy–imine ligated metal complexes have recently attracted great interest both in academia and in industry. It is expected that future research on phenoxy-based olefin polymerization catalysts will provide opportunities to synthesize additional polyolefinic materials with unique microstructures and related properties.

III. Conclusion

It is now clear that the advent of phenoxy-based high performance catalysts for the polymerization of olefins has initiated a revolution in the fields of polymerization catalysis and polymer synthesis.

Quite a few highly-active catalysts featuring phenoxy-based ligands are available for the polymerization of ethylene, α-olefins, dienes and others. In addition, phenoxy-based catalysts have now been disclosed that produce a variety of unique polymers, such as vinyl-terminated low molecular weight polymers, ultra-high molecular weight polymers, high molecular weight amorphous α-olefin copolymers, functionalized polymers, well-defined multimodal polymers and regio- and stereo-irregular high molecular weight polymers. Moreover, high-performance living polymerization catalysts with phenoxy-based ligands have been introduced, some of which are capable of combining living enchainment with control of polymer stereochemistry. In consequence, new classes of polyolefinic block copolymers having various crystalline and amorphous segments as well as many monodisperse polymers with high stereoregularity and/or high molecular weights have been created.

Therefore, phenoxy-based transition metal polymerization catalysts have been widening the scope of polyolefinic materials accessible by transition metal-based catalytic technology. We believe that phenoxy-based catalysts will continue to generate interest in both industrial and academic research laboratories because of their high catalyst efficiency and their ability to produce a wide range of distinctive polymers previously unobtainable with conventional catalysts. It is safe to conclude that the phenoxy-based catalyst family will continue to be a rich source for the development of a new generation of olefin polymerization catalysts.

We would like to thank Drs. M. Mullins and A. Valentine for fruitful discussions and suggestions. We are grateful to Prof. S. T. Nguyen for giving us some important information about his ongoing research.

Abbreviations

AFM: atomic force microscopy
b: block
Bn: benzyl
CGC: constrained-geometry catalysts
Cp: cyclopentadienyl
C_p*: pentamethylcyclopentadienyl
DFT: density functional theory
$\Delta G^{\#}$: activation Gibbs free energy
EPR: ethylene/propylene rubber
iPP: isotactic polypropylene

Table 2. Catalysts Categorized Accoding to the Polymer Products

	Homopolymerizaiton			Copolymerization	
		Stereoselective	Living	Random, with Ethylene	Block
Ethylene	**1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23, 24, 25, 26, 28, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 66, 67, 68, 69, 70, 71, 72, 73**		**14**		**14**
Propylene	**2, 3, 6, 14, 25, 47, 49, 50, 59, 65**	**14, 25, 27, 65, 73, 78**	**14**	**3, 11, 14, 26, 29, 30, 56**	**14**
Higher α-Olefins	**3, 6, 14, 25, 59, 74, 75, 78**	**51, 78**	**3, 76, 78**	**3, 5, 14, 16, 35, 41, 48, 49, 50, 67**	**76**
Cycloolefins	**6, 14, 35, 72**			**14, 35**	**14**
Styrene	**1, 3, 35, 47, 59**	**14, 59**		**3, 52, 59, 62**	
Butadiene	**49, 50, 51, 59**			**14**	
Polar Comonomers				**35, 50**	

m: meso
MAO: methylaluminoxane
M_n: number-average molecular weight
M_v: viscosity-average molecular weight
M_w: weight-average molecular weight
NMR: nuclear magnetic resonance
PE: polyethylene
PP: polypropylene
PS: polystyrene
r: racemo
SHOP: Shell higher-olefins process
sPP: syndiotactic polypropylene
sPS: syndiotactic polystyrene
TEM: transmission electron microscopy
T_m: melting temperature
TOF: turnover frequency
TON: turnover number

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Yasuhiko Suzuki was born in November 1966 in Niigata, Japan. He received his bachelor's and master's degrees in synthetic chemistry from Kyoto University. He Joined Mitsui Petrochemical Industries (now Mitsui Chemicals, Inc.) in 1991 as a researcher. His research interests include synthetic organic chemistry, organometallic chemistry, and olefin polymerization catalysts.

Hiroshi Terao was born in February 1973 in Nagoya, Japan. He graduated from the University of Tokyo in 1996, and completed his Ph.D. in physical organic chemistry under the supervision of Prof. Tadashi Sugawara in the graduated school of arts and sciences at the University of Tokyo in 2001. He joined Mitsui Chemicals, Inc. as a researcher where he is working on the development of new olefin polymerization catalysts. His research interests include physical organic chemistry, organometallic chemistry, and olefin polymerization catalysts.

Terunori Fujita was born in November 1957 in Ehime, Japan. He received his bachelor's and master's degrees in chemistry, natural product synthesis, from Hokkaido University working with Professors Takeshi Matsumoto and Haruhisa Shirahama. He obtained his Ph.D. degree in organic chemistry, anion coordination chemistry, from l'Université Louis Pasteur de Strabourg, France, in 1988 with Professor Jean-Marie Lehn. He joined Mitsui Petrochemical Industries, Ltd. (now Mitsui Chemicals, Inc.) in 1982, where he is now one of the four research fellows. Since 1988 his research interests have been focused on "synthesis of valuable organic materials with high efficiency using homogeneous and heterogeneous catalysis." Most recently, he has been working on the development of highly-active olefin polymerization catalysts and their applications for the preparation of polymers with new or enhanced material properties. He is a recipient of the Catalysis Society of Japan Award for Young Researchers for 2001 and the JLPO Award (Italy) in 2002.