

## FI Catalysts for Olefin Polymerization—A Comprehensive Treatment

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## 1. INTRODUCTION

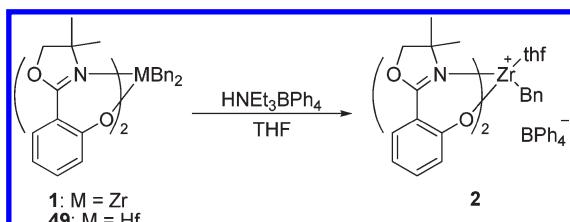
### 1.1. General Overview

Polyolefinic materials, exemplified by polyethylenes (PEs), polypropylenes (PPs), and ethylene/ $\alpha$ -olefin amorphous copolymers, display many notable properties; namely, they are lightweight and possess excellent mechanical strength, flexibility, processability, chemical inertness, and recyclability. This makes them very cost-effective. It is no surprise then that polyolefinic materials are used in the manufacture of numerous products, such as toys, notebook holders, shopping bags, food packages, shampoo and detergent bottles, storage boxes, disposable diapers, sneakers, outdoor-indoor carpets, bullet-proof vests, fuel tanks, and car bumpers.<sup>1–3</sup> In other words, these materials play a direct role in everyday life. Naturally, therefore, polyolefinic materials are the most used synthetic polymers today, and the worldwide consumption of these materials exceeded 100 million tons in 2005.<sup>4</sup>

The discovery of Ziegler–Natta catalysts (a binary mixture of a titanium halide species and an organo-aluminum compound) in the 1950s launched the production of high-density PEs and isotactic PPs (iPPs), a catalytic revolution for which Ziegler and Natta won the Nobel Prize in Chemistry in 1963.<sup>5</sup> Since this discovery, a tremendous amount of academic and industrial research has been devoted to the development of higher performance olefin polymerization catalysts due to the importance of polyolefinic materials. Although the majority of commercially available polyolefinic materials are still produced with heterogeneous, multisited Ziegler–Natta catalysts (as represented by  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts), products from highly active single-site group 4 metallocene catalysts (metallocene catalysts) that were originally reported by Kaminsky and co-workers in 1980,<sup>6</sup> and which include a combination of group 4 metallocenes and methylaluminoxane (MAO), are today becoming more prevalent in the marketplace.

Unlike  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts, metallocene catalysts possess a well-defined active site that permits control over polymer molecular weight, molecular weight distribution, comonomer incorporation, and polymer stereochemistry, resulting in the formation of a wider range of differentiated polyolefinic materials with new or enhanced performance qualities.<sup>7–12</sup> Metallocene catalysts thus initiated the commercial production of high-performance linear low-density PEs, iPPs, syndiotactic PPs (sPPs), ethylene/1-butene amorphous copolymers, ethylene/propylene diene elastomers, and others. Additionally, and importantly, metallocene catalysts are molecular catalysts and, hence, have provided systematic opportunities to study the mechanisms of the initiation, propagation, and termination steps of coordination polymerization and the mechanisms of stereoselective polymerization, which has significantly contributed to advances in the rational design of catalysts for controlled olefin (co)polymerization. Particularly notable is the development of chiral stereorigid ansa-metallocenes by Brintzinger, Ewen, and their co-workers regarding the production of highly isotactic and syndiotactic PPs by rational catalyst design based on an understanding of stereoregulating mechanisms.<sup>13,14</sup> Altogether, the development of metallocene catalysts has had a dramatic impact on polymer synthesis and catalysis chemistry. Therefore, great interest has been shown in the development of new single site catalysts (post-metallocene catalysts) capable of providing novel olefin-based materials, as well as higher catalyst productivity, and greater control over polymer microstructures. As a consequence of a formidable amount of both academic and industrial research, a large number of new high-activity single site catalysts based on a wide array of early and late transition metals have been discovered.<sup>15–18</sup> Some of these new catalysts have enabled us to prepare distinctive polymers such as hyperbranched PEs, ethylene/methyl acrylate copolymers, and  $\alpha$ -olefin-based block copolymers, which are either difficult or practically impossible to produce using metallocene catalysts. Therefore, post-metallocene catalysts have broadened the range of olefin-based materials accessible by transition metal-based catalytic technology. In the late 1990s, this trend incidentally led three groups to independently discover that certain salicylaldimine (phenoxy–imine) compounds could serve as an excellent ligand for olefin insertion polymerization catalysts with early (Fujita at Mitsui Chemicals, 1997)<sup>19</sup> and late transition metals (Johnson at DuPont<sup>20</sup> and Grubbs at Caltech,<sup>21,22</sup> both in 1997). These discoveries invoked renewed interest on this conventional and yet versatile ligand motif and spurred intense research into the phenoxy–imine ligand and its associated chemistry around the globe.

Scheme 1



### 1.2. Phenoxy–Imine Catalysts with Early Transition Metals

Bis(phenoxy–imine) early transition metal complexes developed by Fujita and co-workers (now known as FI catalysts) constitute a unique family of new generation olefin polymerization catalysts. FI catalysts, when activated, exhibit unprecedented catalytic activities for the polymerization of ethylene. In fact, prior to their work, metallocene catalysts were the most active catalysts for ethylene polymerization, but now many FI catalysts display substantially higher activities than metallocene catalysts.<sup>23–27</sup>

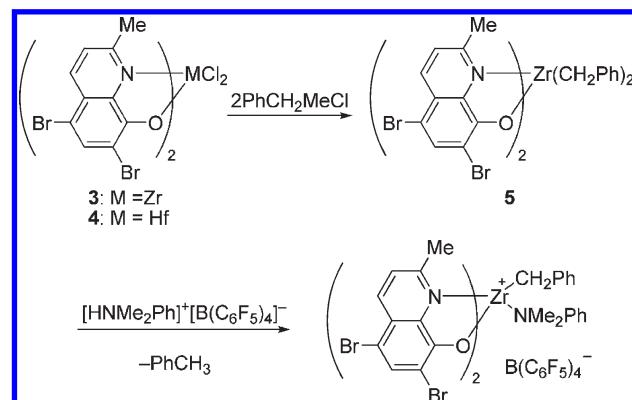
The discovery of FI catalysts was actually preceded by a long embryonic period and can be traced back to more than 30 years ago. Around that time, the mechanistic aspects of heterogeneous Ziegler catalysts were a focus of attention in the field and there was a dispute if the heterogeneity of Ziegler catalysts could be a cause of their high activity. In the late 1950s, Natta and Breslow examined olefin polymerization using titanocene ( $Cp_2TiCl_2$ ) with alkylaluminums as a soluble model of the Ziegler catalysts.<sup>28–31</sup> In the 1980s, the study on metallocenes was rejuvenated with the discovery of MAO, which eventually led to the so-called “metallocene revolution”<sup>7,10–12,32,33</sup>

Around the same time as Natta and Breslow, Taylor examined several phenoxy–azo and phenoxy–imine chelating compounds in combination with  $TiCl_4$  in search for another soluble version of the Ziegler catalysts.<sup>34</sup> It was found that some chelating agents simply deactivated active heterogeneous  $TiCl_4/Et_2AlCl$  catalysts at higher molar ratios of chelate to Ti above 0.5–1, where the reaction mixture became soluble. However, some chelating agents caused an initial drop in activity followed by an increase at a particular chelate/Ti ratio, implying that chelated Ti complexes may serve as a soluble Ziegler catalyst. This might be the first example of FI catalysts, which were generated *in situ*. However, this chemistry was not pursued any further and the possibility of success was missed for more than 30 years.

Chelate complexes of vanadium are another class of soluble Ziegler catalysts that have been the subject of intensive academic and industrial research for a long time. For these soluble vanadium catalysts,  $\beta$ -diketones have been typically used as a chelating agent. Milani and Doi examined phenoxy–imine ligands with vanadium but found that they were not any better than conventional  $\beta$ -diketones.<sup>35,36</sup>

Pioneering research on structurally related group 4 transition metal complexes was performed by Floriani, Jordan, and their co-workers. In 1995, Cozzi and Floriani demonstrated that a cationic complex 2 derived from the benzyl complex 1 featuring phenoxy–oxazoline ligands and  $HNEt_3BPh_4$  functions as a catalyst for the polymerization of ethylene without the need for an activator, albeit at a very low rate (0.12 g-polymer/(mmol·M·h)) (Scheme 1).<sup>37,38</sup> Additionally, Bei and Jordan reported on the structures and ethylene polymerization behavior of Zr and Hf complexes 3 and 4, bearing 8-quinolinoxy ligands in 1997. They also showed that, in combination with  $HNMe_2Ph(B(C_6F_5)_4)/Bu_3Al$ , the benzyl complex 5, possessing brominated ligands, is active for ethylene polymerization

Scheme 2



(max. 41 g-polymer/(mmol·M·h)) whereas those with nonbrominated ligands are inactive, demonstrating the substituent effect on catalytic activity (Scheme 2).<sup>39</sup>

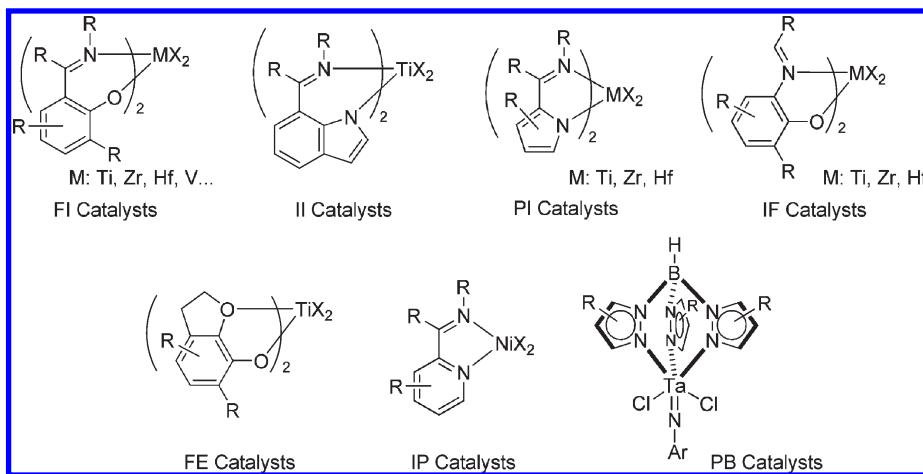
Tetradentate  $[O,N,N,O]$  ligands such as salen, salphen, acen, and their derivatives have also been examined in combination with early metals of groups 4 and 5 by many groups. Some of the tetradentate ligands forced the coordination complexes to adopt a structure where two nonspectator ligands such as chloride, that become reagent and substrate ligands upon activation, are trans to each other. They were obviously not suitable for olefin insertion chemistry to a M–alkyl bond and showed low polymerization activity. Therefore, tetradentate ligands that allowed cis chlorides or alkyls were designed and synthesized, but they exhibited only low to moderate activity for ethylene polymerization.<sup>40–44</sup>

Against this background, Fujita and co-workers carried out research based on a ligand oriented catalyst design concept, a concept that is founded on the Mitsui-held belief that the flexible electronic nature of a ligand is a key requirement for achieving high activity. This is because DFT calculations performed on a model metallocene catalyst  $H_2SiCp_2ZrMe^+$  for ethylene polymerization suggested that ethylene polymerization is a process that involves intense electron exchange between a ligand and a metal.

The research based on the ligand oriented catalyst design concept that emphasizes the flexible electronic nature of a ligand<sup>23,24,26,27,45,46</sup> has resulted in the discovery of a number of highly active catalysts for the polymerization of ethylene, including phenoxy–indenyl ligated group 4 transition metal complexes,<sup>47</sup> which represent the first examples of high performance olefin polymerization catalysts incorporating phenoxy/Cp-based ligands, phenoxy–imine ligated early transition metal complexes (FI catalysts), indolide–imine ligated Ti complexes (II catalysts),<sup>48,49</sup> pyrrolide–imine ligated group 4 transition metal complexes (PI catalysts),<sup>50–55</sup> imine–phenoxy ligated group 4 transition metal complexes (IF catalysts),<sup>56,57</sup> phenoxy–ether ligated Ti complexes (FE catalysts),<sup>58</sup> imine–pyridine ligated Ni complexes (IP catalysts),<sup>59</sup> and tris(pyrazolyl)borate ligated Ta complexes (PB catalysts)<sup>60</sup> (Figure 1).

### 1.3. Phenoxy–Imine Catalysts with Late Transition Metals

On the other hand, mono(phenoxy–imine) nickel complexes have been developed on the basis of two important precedent technologies: (1) ethylene oligomerization catalysts based on  $[P, O]$  chelated Ni complexes (Shell's higher olefin process)<sup>61,62</sup> and (2) Ni and Pd diimine olefin polymerization catalysts developed by Brookhart.<sup>16,63,64</sup> The phenoxy–imine ligands provide a suitable steric environment to block the axial faces of the Ni



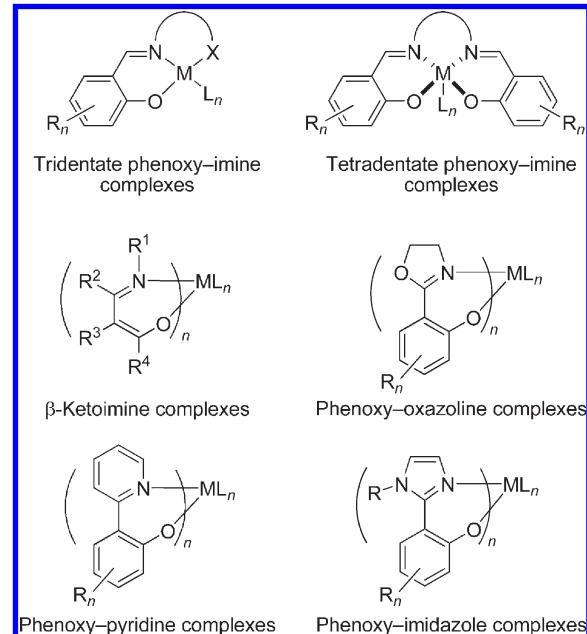
**Figure 1.** Examples of highly active ethylene polymerization catalysts discovered on the basis of the ligand oriented catalyst design concept.

center by introducing bulky substituents at the imine nitrogen and ortho to the phenolic oxygen, which resembles the catalyst design established by the diimine catalysts for square planar complexes to effectively prevent the chain transfer reaction via  $\beta$ -H elimination, thus allowing the formation of high molecular weight polymers. In addition, the most notable feature of the phenoxy-imine Ni complexes is that they are neutrally charged in their activated forms and therefore believed to possess even more enhanced tolerance toward polar functional groups than the diimine nickel or palladium complexes, which form cationic species upon activation. Due to the tolerance to polar functions, the phenoxy-imine Ni complexes were used in the copolymerization of ethylene and polar functional comonomers<sup>65</sup> and dispersion/emulsion polymerizations in polar media, for example, water<sup>66–75</sup> or liquid CO<sub>2</sub>.<sup>76–78</sup>

#### 1.4. Scope of This Review

As described above, these two phenoxy-imine catalysts possessing early and late metals were developed quite independently with different technological histories and with quite different rationales and motives. However, one can also say that they have many things in common. For example, there is no doubt that both catalysts have benefited from unique ligand properties, that is, ease of synthesis and amenability to structural/electronic modifications, which results in extremely rich and diverse ligand libraries. Moreover, phenoxy-imine ligands can act on different metals over a wide range of the periodic table, making superb olefin polymerization catalysts, and this, along with the fact that a very similar ligand design (position, size, and nature of substituents) was often used in order to maximize the catalytic performance despite the difference in metal centers, was what prompted us to write this comprehensive treatment in the first place. Thus, this review will deal with olefin insertion polymerization catalysts based on any metal if they bear phenoxy-imine or related ligands dating from 1950. More specifically, phenoxy-imine and related ligands in this review are defined as a class of [N=C—C=O] compounds, which form a six-membered chelate ring with a metal center (Figure 2).

A survey of the complexes that fulfilled the definition above, and were used for olefin polymerization, has revealed that more than 500 scientific articles have been written on the subject since 1964. Of these, phenoxy-imine ligands were employed in 77% of the publications, most of which appeared after 1999. The



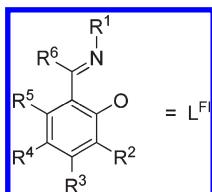
**Figure 2.** Examples of the complexes with phenoxy-imine-related ligands dealt with in this review.

upsurge in phenoxy-imine catalyst study actually inspired research on similar  $\beta$ -ketoimine ligands, on which an increasing number of reports have also appeared (14%, counted twice if it includes two classes of complexes). The chelation, other than phenoxy-imine or  $\beta$ -ketoimine, includes phenoxy-pyridine, phenoxy-oxazoline, phenoxy-imidazole, etc., collectively reaching a total of 9%. The phenoxy-imine ligand can be further classified into bridged tetradentate [O,N,N,O] ligands including classical salen and salphen (13%), and tridentate [O,N,X] or [O,N,L] phenoxy-imine ligands (8%) that have another pendant donor group (X or L), in addition to ordinary bidentate [O,N] phenoxy-imine ligands (50%).

Regarding the metal center, Ti complexes have been investigated most intensively in 34% of the publications, followed by Ni complexes (25%) and Zr complexes (20%). Less investigated metals below 5% each are V, Hf, Pd, Co, and Cr, and several more exist.

In the following sections, these complexes are classified primarily by the ligand structure, secondarily by metals, and finally by olefins for polymerization. Heterogenization of the

Chart 1



complexes for practical use and various unique olefin-based materials, many of which were previously unavailable via other means of polymerization, are also discussed.

## 2. SYNTHESIS OF PHENOXY-IMINE COMPLEXES

One of the favorable characteristics of the phenoxy-imine ligand motif is their ease of synthesis. Phenoxy-imine ligands can be synthesized by straightforward Schiff base condensation of amines and phenolic compounds bearing carbonyl groups, both of which can be purchased as commercially available chemicals or readily prepared from them. Each step of the synthesis in most cases involves well-established reactions, such as Friedel-Crafts alkylation, ortho-formylation, Schiff base condensation, etc. This straightforward synthesis, along with rich inventories of starting chemicals, resulted in a tremendous structural diversity of phenoxy-imine ligands, which in some instances allowed quick identification of promising lead complexes via high throughput screening. In addition, this structural diversity, combined with the well-defined nature of phenoxy-imine ligated complexes, has enabled extensive and systematic studies to establish structure-reactivity relationships in olefin polymerization mediated by these catalysts.

In this section, the synthesis of phenoxy-imine ligands and their complexation with various metal sources (metalation) are summarized with respect to each substituent and each metal. The substituents of a phenoxy-imine ligand are numbered from  $R^1$  to  $R^6$  as shown in Chart 1, and hereafter we will occasionally use the notation ( $L^{FI}$ )<sup>-</sup> as the generic form for phenoxy-imine ligands,  $1\text{-}(R^1\text{N}=\text{CR}^6)(C_6\text{R}^2\text{R}^3\text{R}^4\text{R}^5)\text{-}2\text{-O}^-$ .

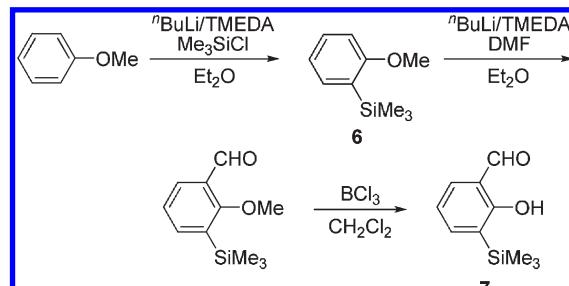
### 2.1. Ligand Synthesis

**2.1.1.  $R^1$  Substituents.** In order to introduce an  $R^1$  substituent, the corresponding primary amine ( $R^1\text{-NH}_2$ ) and appropriate 2-hydroxybenzaldehydes should furnish the desired phenoxy-imine compound in high yields. In general, Schiff base condensation with salicylaldehydes and aliphatic amines is fast and proceeds without any problem at room temperature. When using aromatic amines (mostly aniline derivatives), the reaction is much slower, particularly for anilines possessing electron-withdrawing substituents. In such cases, heating and/or adding a small amount of an acid (for example, formic acid, acetic acid, and *p*-toluene sulfonic acid) as a catalyst accelerates the reactions to completion. Alternatively, Coates and co-workers synthesized phenoxy-imine ligands having an electron-withdrawing pentafluorophenyl group as  $R^1$  substituents by using *N*-sulfinylpentafluoroaniline, which was prepared from pentafluoroaniline and thionyl chloride, and salicylaldehydes to afford the desired phenoxy-imine ligands.<sup>79</sup>

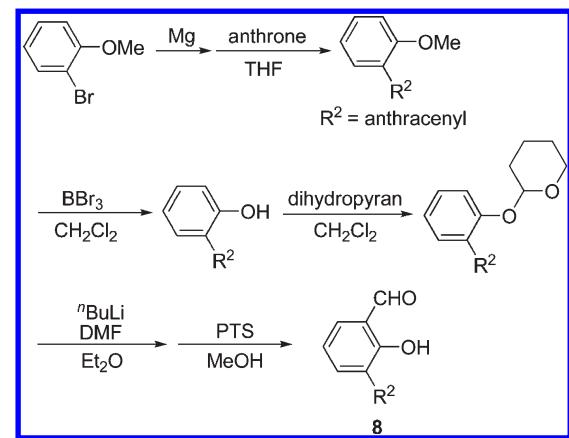
In one example in synthesizing phenoxy-imine Ni(II) complexes, Schiff base condensation was carried out between amines and the Ni complexes ligated by salicylaldehydes, affording the desired bis(phenoxy-imine)nickel(II) complexes.<sup>80</sup>

**2.1.2.  $R^2$  Substituents.** Introduction of  $R^2$  substituents requires ortho- $R^2$ -substituted phenols as a starting material, followed by ortho-formylation of the phenols to prepare the corresponding

Scheme 3



Scheme 4



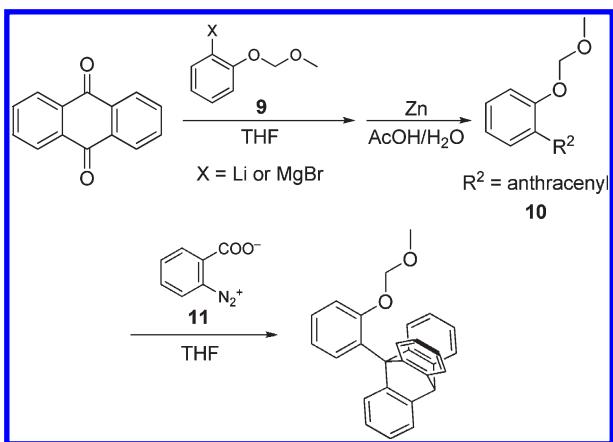
salicylaldehydes. Although there are many commercially available *ortho*-alkylphenols, they are conveniently prepared by the electrophilic substitution (Friedel-Crafts alkylation) of phenols. For example, 2-cyclohexyl-4-methylphenol was prepared from *p*-cresol and chlorocyclohexane using aluminum chloride as a catalyst.<sup>81,82</sup> Similarly, cyclooctyl and cyclododecyl derivatives were prepared by cyclooctene or cyclododecene and *p*-cresol in the presence of a small amount of concentrated sulfuric acid as a catalyst.<sup>83</sup>

When applying the alkylsilyl group as  $R^2$  substituents, ortholithiated anisole and  $\text{Me}_3\text{SiCl}$  afforded 2-Me<sub>3</sub>Si-anisole **6**, which was followed by standard ortho-formylation and demethylation by  $\text{BCl}_3$ , furnishing the desired salicylaldehyde **7** (Scheme 3).<sup>84,85</sup> A similar method was applied for the synthesis of naphthol-imine ligands that have the triphenylsilyl group as  $R^2$  substituents.<sup>86</sup>

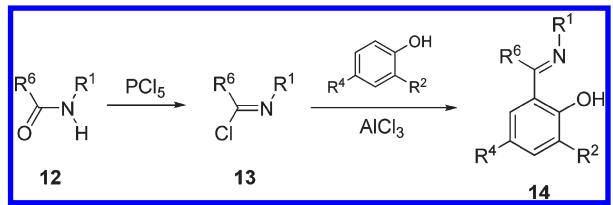
Toward the bulkier  $R^2$  substituents, 3-anthracylsalicylaldehyde **8** was successfully synthesized from anthrone and 2-bromoanisole, whose hydroxyl group was protected by the tetrahydropyran (Scheme 4).<sup>87</sup> Gibson and co-workers also reported on the synthesis of 9-(2-methoxymethoxy-phenyl)anthracene **10** from anthraquinone and ortho-metalated (Li or MgBr) phenol **9**. The anthracenyl group was transformed into the triptyceny group by reacting with benzyne, which was generated *in situ* from diazo-benzenecarboxylate **11** (Scheme 5).<sup>88</sup>

**2.1.3.  $R^6$  Substituents.** In order to have a desired  $R^6$  substituent, Schiff base condensation with an appropriate ketone instead of an aldehyde is one possible employable method; however, the reaction is often too slow to obtain the desired phenoxy-ketimine ligand. Coates and co-workers reported that a variety of phenoxy-ketimine ligands **14** ( $R^6 = \text{Me, Et, Ph, CF}_3, \text{Pr, cyclohexyl, cyclopentyl, 1-naphtyl, 2-naphtyl, 4-methoxyphenyl, mesityl}$ ,

Scheme 5



Scheme 6



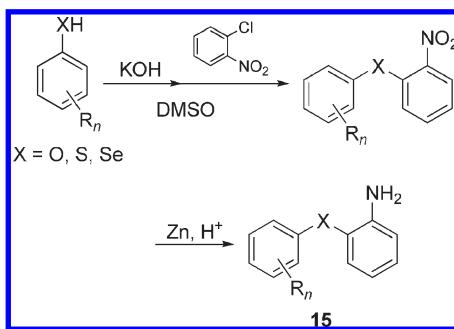
$C_6F_5$ ) could be prepared via the Friedel–Crafts reaction of phenol derivatives with imidoyl chlorides **13**, which were formed in situ from the corresponding amides **12** and  $PCl_5$  (Scheme 6).<sup>89–91</sup> Lu, Guo, and Mazzeo and their co-workers used similar methods to introduce Me, Et, 2-methylphenyl, 2-fluorophenyl, 2-chrolophenyl, 2-bromophenyl,<sup>92–94</sup> and Ph groups.

**2.1.4. Tridentate [O,N,L] or [O,N,X] Ligands.** Most of the tridentate phenoxy-imine ligands synthesized so far possess an extra donor atom on  $R^1$ , and therefore, primary amines with an extra donor would be an essential starting material. Examples include pyridin-2-ylmethanamine,<sup>86,88,95–99</sup> quinolin-8-amine,<sup>86,95,98,100</sup> and *N,N*-dimethylethylenediamine<sup>95</sup> as N-containing primary amines; 2-phenoxyaniline<sup>95,101–103</sup> and 2-methoxyaniline<sup>102,104–106</sup> as O-containing primary amines; 2-aminothiophenol<sup>98,103,107</sup> as S-containing primary amines; and 2-diphenylphosphinoaniline<sup>95,98,108,109</sup> as P-containing primary amines. Additionally, 9-aminofluorene,<sup>110</sup> amino acids,<sup>111</sup> and 2-aminomethyl-1-methylbenzimidazole dihydrochloride<sup>112</sup> were also employed as a primary amine possessing an extra coordinating donor.

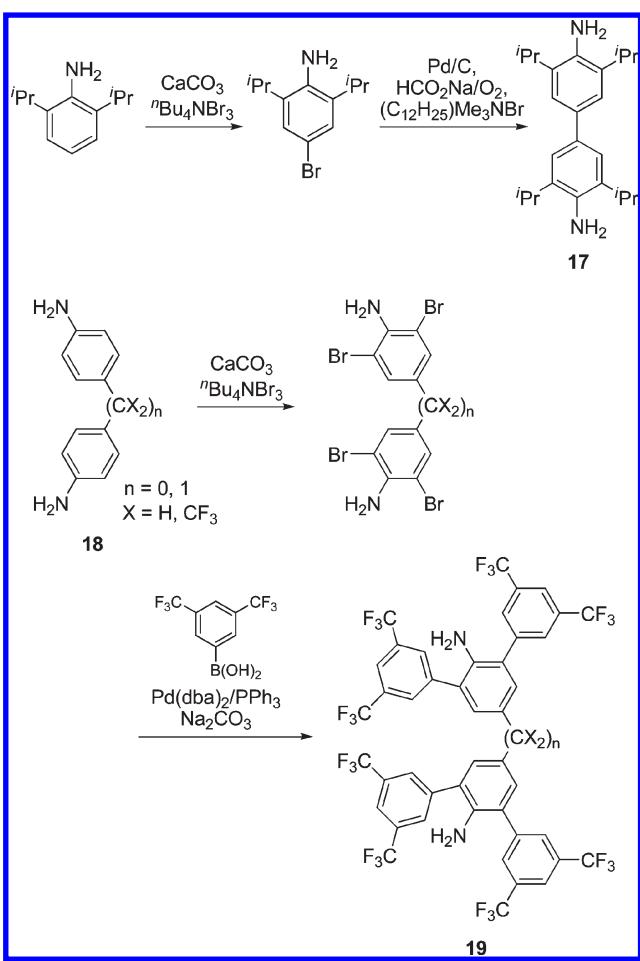
In addition to these commercially available amines, *ortho*-E-anilines (**15**, E: aryloxy; arylthio; arylselanyl) were prepared from 1-chloro-2-nitrobenzene<sup>113–116</sup> and appropriate phenols, qbenzenethiols, or benzeneselenols in the presence of 1 equiv of KOH and successive reduction of  $NO_2$  by Zn/HOAc (Scheme 7). Reaction between a phenoxy-imine ligand, whose  $R^1$  substituent was the 2-bromoethyl group, and 1-isopropyl-1*H*-imidazole furnished imidazolium bromide as  $R^1$ , which, upon complexation, afforded Ni complexes bearing N-heterocyclic carbene (NHC) as a pendant extra donor at the  $R^1$  substituent (Chart 21, **16**).<sup>117</sup>

**2.1.5. Ligands for Multinuclear Complexes.** For synthesis of multinuclear complexes that have more than two phenoxy-imine ligated metal moieties in one molecule, it is necessary to

Scheme 7



Scheme 8



synthesize a ligand which has two or more phenoxy-imine units covalently linked together. Such ligands can be obtained simply by using appropriate bifunctional starting materials, and the rest of the synthesis will be similar to that of monofunctional phenoxy-imine ligands. The most common approach is to use appropriate diamines, resulting in covalent linking groups at  $R^1$ .<sup>75,77,118–124</sup> Care must be taken when designing the linking groups so that formation of tetradentate mononuclear complexes can be avoided. Mecking and co-workers synthesized such diamines, 2,2',6,6'-tetraisopropylbiphenyl-4,4'-diamine **17** from 2,6-diisopropylaniline via bromination and subsequent palladium-catalyzed

oxidative coupling (Scheme 8).<sup>75</sup> Di(2,6-diarylanilines) linked directly or via  $-\text{CH}_2-$  or  $-\text{C}(\text{CF}_3)_2-$  at para positions (**19**) were synthesized by the bromination of the corresponding di(anilines) **18** followed by Suzuki coupling with 3,5-bis(trifluoromethyl)-phenylboronic acid (Scheme 8).<sup>75,77</sup>

These  $\text{R}^1$  linked phenoxy-imine ligands possibly resulted in the formation of macrocyclic complexes of the type  $(\text{L}^{\text{FI}}-\text{L}^{\text{FI}})_2-(\text{MX}_n)_2$ .<sup>125-127</sup>

Another approach for multinuclear phenoxy-imine complexes is to connect the phenol moiety, that is, to use biphenyl-2,2'-diol (for example, complex **20** in Chart 27)<sup>128-130</sup> or naphthalene-1,8-diol (for example, complexes **21** and **22** in Scheme 22).<sup>131-134</sup>

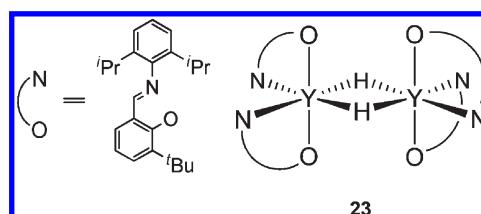
The use of 2-hydroxysophthalaldehyde and certain amines furnished  $[\text{N},\text{O},\text{N}]$  type tridentate ligands, which can bind nickel metals in different ways depending on the ligand structures, affording different multinuclear complexes.<sup>119,135</sup> With  $\text{Zr}(\text{O}^{\text{i}}\text{Pr})_4$  and 2,6-diimine-phenol compounds, a mononuclear complex having *trans*-N/*trans*-O/*trans*-O' $\text{Pr}$  was obtained and characterized.<sup>136</sup> Finally, when both the imine and the phenol moieties are bifunctional, metallocopolymers can be synthesized.<sup>137</sup>

## 2.2. Metalation

Complexation of phenoxy-imine or related ligands and a metal source requires a lot of consideration when obtaining the desired metal complexes. In many instances, choice of the metal sources will determine the nonspectator ligands (X and L) of the resulting complexes. Therefore, metal sources should be chosen having regard to the fact that these nonspectator ligands can have a significant influence on the activation process and also that the nucleophilicity of L may have a large impact on the stability of the complexes as well as the catalytic efficiencies during polymerization. Structures of ligands are often decisive in achieving the desired composition of the ligands and the metal center; namely, sterically less demanding ligands tend to form a complex that bears more ligands than desired, which sometimes leaves no reactive sites for polymerization. The nucleophilicity of the phenoxy-imine ligands also has an impact on the composition of the complexes. Phenoxy-imine ligands can be used as  $(\text{L}^{\text{FI}})-\text{H}$ ,  $(\text{L}^{\text{FI}})\text{M}'$  ( $\text{M}'$ : alkali metals), or  $(\text{L}^{\text{FI}})-\text{SiR}_3$  depending on the metal sources employed. The metalation processes yield the desired complexes with a concomitant formation of acids, alkanes, alcohols, amines, silyl halides, and alkali salts, as by-products, which need to be readily and completely removed, for example, by filtration or evacuation to obtain sufficiently pure complexes. When the liberation of acids is expected, the metalation was often carried out in the presence of inorganic/organic bases. With these general considerations in mind, we will discuss hereafter the metalation processes for each metal.

**2.2.1. Group 3 Metals.** Bochmann and co-workers reported on the synthesis of Sc and Y complexes.<sup>138</sup> The reactions between lithium or sodium salts,  $(\text{L}^{\text{FI}})\text{M}'$  ( $\text{M}' = \text{Li}, \text{Na}$ ) and  $\text{MCl}_3(\text{thf})_3$  ( $\text{M} = \text{Sc}, \text{Y}$ ) resulted in a mixture of products. However, alkane elimination between neutral ligands,  $(\text{L}^{\text{FI}})-\text{H}$ , and  $\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_3$  at  $-20^\circ\text{C}$  successfully afforded the desired product,  $(\text{L}^{\text{FI}})\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ . Similarly, by employing a bulkier and more stable metal source,  $\text{M}(\text{CH}_2\text{SiMe}_2\text{Ph})_3(\text{thf})_2$ , Piers and co-workers successfully obtained  $(\text{L}^{\text{FI}})_2\text{M}(\text{CH}_2\text{SiMe}_2\text{R})$  ( $\text{M} = \text{Sc}, \text{Y}; \text{R} = \text{Me}, \text{Ph}$ ) from 2 equiv of  $(\text{L}^{\text{FI}})-\text{H}$  and  $\text{M}(\text{CH}_2\text{SiMe}_2\text{R})_3\text{L}_2$ .<sup>139</sup> These complexes were hydrogenated into  $\mu$ -hydride complexes (for example, complex **23**; Chart 2) under 0.4 MPa of hydrogen, which were then tested as ethylene polymerization catalysts. Longo and co-workers prepared

Chart 2



a Sc complex,  $(\text{L}^{\text{FI}})\text{ScCl}_2(\text{thf})$  ( $\text{R}^1 = 8\text{-quinolinyl}, \text{R}^2 = {^t}\text{Bu}$ ), by adding  $\text{ScCl}_3$  to a reaction mixture of  $(\text{L}^{\text{FI}})-\text{H}$  with  ${^t}\text{BuOK}$ .<sup>140</sup> Yao and co-workers also synthesized and characterized dimeric Ln complexes bearing tridentate  $\beta$ -ketoimine ligands via salt elimination using sodium salts of ligands and  $\text{LnCl}_3$  ( $\text{Ln}: \text{Y}, \text{Yb}, \text{Tb}$ ).<sup>141</sup>

**2.2.2. Group 4 Metals.** As summarized in Table 1, the most commonly employed metal sources are  $\text{TiCl}_4$  and  $\text{ZrCl}_4(\text{thf})_2$  for the synthesis of titanium and zirconium complexes, respectively. When  $\text{MCl}_4$  or  $\text{MCl}_4(\text{thf})_2$  are used as metal sources, phenoxy-imine ligands are deprotonated in advance and employed as alkali metal salts. Although  $^t\text{BuLi}$  is commonly used for preparation of a lithium salt, Erker and co-workers prepared a Li salt with lithium diisopropylamide (LDA) to prepare O-lithiated hydroxyferrocene carbaldimine precursors.<sup>142,143</sup> Sodium or potassium salts can be conveniently prepared by alkali hydrides such as  $\text{NaH}$  and  $\text{KH}$ . Pellcchia and co-workers prepared a Ti salt of a tridentate phenoxy-imine ligand by treating  $(\text{L}^{\text{FI}})-\text{H}$  with  $\text{TiOEt}$ , after which the obtained  $(\text{L}^{\text{FI}})\text{Ti}$  was reacted with  $\text{MCl}_4(\text{thf})_2$  ( $\text{M}: \text{Ti}, \text{Zr}, \text{Hf}$ ) to afford  $(\text{L}^{\text{FI}})\text{MCl}_3$ .<sup>100</sup> Although addition of  $(\text{L}^{\text{FI}})-\text{H}$  to  $\text{MCl}_4$  often gives the desired products via elimination of  $\text{HCl}$ , it sometimes results in the imine-protonated complexes  $(\text{L}^{\text{FI}}\text{H}^+)_2\text{MCl}_4$ .<sup>144</sup> In such cases, metalation can be carried out in the presence of an organic base such as triethylamine to prevent the imine protonation,<sup>42,144</sup> or the isolated  $(\text{L}^{\text{FI}}\text{H}^+)_2\text{MCl}_4$  was deprotonated afterward by adding triethylamine to afford  $(\text{L}^{\text{FI}})_2\text{MCl}_2$  (**24**) (Scheme 9).<sup>144</sup>

Metal sources other than chlorides ( $\text{MX}_4, \text{X} = \text{CH}_2\text{Ph}, \text{OR}, \text{NR}_2, \text{R} = \text{alkyl}$ ) can also be used with  $(\text{L}^{\text{FI}})-\text{H}$  to afford  $(\text{L}^{\text{FI}})_2\text{MX}_2$  via the elimination of alkane, alcohol, and amine ( $\text{X}-\text{H}$ ). When alkoxides or amides are used as precursors, less efficient alkylation of  $\text{M}-\text{X}$  bonds in  $(\text{L}^{\text{FI}})_2\text{MX}_2$  ( $\text{X} = \text{OR}, \text{NR}_2$ ) (compared to the chlorides that are normally used), or other complications due to the residual functionality of X groups in coproducts of the alkylation, may cause apparently lower catalytic activity.<sup>145</sup> Therefore, chlorination was often attempted using, for example,  $\text{Me}_3\text{SiCl}$  to excess. Erker,<sup>144</sup> Repo,<sup>146,147</sup> and their co-workers prepared  $(\text{L}^{\text{FI}})_2\text{M}(\text{NMe}_2)_2$  via a reaction with  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) and  $(\text{L}^{\text{FI}})-\text{H}$ ; then, they obtained  $(\text{L}^{\text{FI}})_2\text{MCl}_2$  in high yield by adding  $\text{Me}_3\text{SiCl}$ . Repo and co-workers also applied this method to the synthesis of biaryl-bridged tetradentate  $[\text{O},\text{N},\text{N},\text{O}]$  phenoxy-imine complexes.<sup>44</sup> Coates and co-workers obtained  $(\text{L}^{\text{FI}})_2\text{Ti}(\text{O}^{\text{i}}\text{Pr})_2$  by mixing  $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$  and  $(\text{L}^{\text{FI}})-\text{H}$ , which was subsequently transformed into  $(\text{L}^{\text{FI}})_2\text{TiCl}_2$  by adding 2 equiv of  $\text{Me}_3\text{SiCl}$ .<sup>148</sup> In addition to  $\text{Me}_3\text{SiCl}$ ,  $\text{BCl}_3$  can also be used for chlorination of  $\text{Ti}-\text{NMe}_2$  bonds.<sup>149,150</sup> Mixed metal sources,  $\text{MCl}_2\text{X}_2$  ( $\text{X} = \text{OR}, \text{NR}_2, \text{R} = \text{alkyl}$ ) can also be employed for metalation, which directly gave metal chlorides,  $(\text{L}^{\text{FI}})_2\text{MCl}_2$ , by allowing them to react with  $(\text{L}^{\text{FI}})-\text{H}$  (See Table 1).

Metallocene dialkyl complexes,  $\text{Cp}'_2\text{MR}_2$  ( $\text{R}$ : alkyl group), can be activated stoichiometrically by perfluoroarylboron-based activators into well-defined cationic species, thus aiding the understanding of catalytically active species and reaction mechanisms

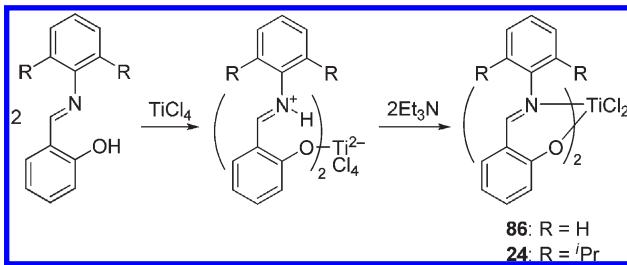
**Table 1.** Synthetic Methods and Metal Sources for the Synthesis of Group 4 Phenoxy–Imine-Related Complexes<sup>a</sup>

Ligand	Ti						Zr						Hf	
	TiCl <sub>4</sub>	TiCl <sub>4</sub> <sup>-</sup> (thf) <sub>2</sub>	TiBn <sub>4</sub>	Ti <sup>-</sup> (NMe <sub>2</sub> ) <sub>4</sub>	TiCl <sub>2</sub> <sup>-</sup> (O <i>i</i> Pr) <sub>2</sub>	ZrCl <sub>4</sub>	ZrCl <sub>4</sub> <sup>-</sup> (thf) <sub>2</sub>	ZrBn <sub>4</sub>	Zr <sup>-</sup> (NMe <sub>2</sub> ) <sub>4</sub>	Zr <sup>-</sup> (O <i>i</i> Pr) <sub>4</sub>	HfCl <sub>4</sub>	HfBn <sub>4</sub>		
bis(phenoxy-imine)	H	94 169	107 Et <sub>3</sub> N 144 <i>n</i> BuLi	147 <i>n</i> BuLi	189 "BuLi	146 "BuLi	147 "BuLi	189 "BuLi	144 Na[N(SiMe <sub>3</sub> ) <sub>2</sub> ]211	144 "BuLi	144 Zr(NMe <sub>2</sub> ) <sub>2</sub> <sup>-</sup> Cl <sub>2</sub> (dme)144	236 "BuLi		
SiMe <sub>3</sub> organicbase	Li													
	44	79	84	190				92	190	212		217		
	85	89	90					204	213	214		235		
	91	94	148					205	215	216		236		
	156	157	158					217	218					
	159	160	161					219	220					
	162	163	164	LDA				221	222					
	165	166	167					142						
	168	194		LDA 143				143						
	Na	149 170	166 171		191			TiMeBr <sub>3</sub> 153 TiCl <sub>2</sub> Me <sub>2</sub> <sup>-</sup> (dme)153	170 207	93 218		236		
	K	H	101	107	101			206	208	223				
	tridentate phenoxy-imine	organicbase	1.11	172		TiOEt 100 112			206	208	223			
	K	H	109	113	114				107		112		112	
tetradentate [O,N,N,O] phenoxy-imine	H	115 43	116 149	172 173	192	149	44	125	127	TiCl <sub>4</sub> 174	176	41	42	41
										TiBr <sub>4</sub> 174	209	151	152	125
										TiI <sub>4</sub> 174		226	227	Zr(NEt <sub>2</sub> ) <sub>4</sub>
												198	198	HfCl <sub>4</sub> (thf)2
SiMe <sub>3</sub> organicbase	Li	178						TiF <sub>4</sub> (thf)2 174						
	Na	40						TiBr <sub>4</sub> 149	209	41				
												210	224	225
														HfCl <sub>4</sub> (thf)4

Table 1. Continued

*a* The numbers appearing in this table correspond to the references.

Scheme 9



in metallocene mediated olefin polymerizations. Metallocene dialkyls are accessible via alkylation of  $\text{Cp}'_2\text{MX}_2$  (X: halogens, OR, NR<sub>2</sub>, etc.) with ordinary alkylating agents, M'—R (M': Li, Mg, Al, Zn, etc.). However, for phenoxy-imine complexes, the reactions with such alkylating agents are in most cases unsuccessful due to the side reactions in reactive imine functional groups. Group 4 metal tetrabenzyl complexes ( $\text{M}(\text{CH}_2\text{Ph})_4$ ) can directly afford  $(\text{L}^{\text{FI}})_2\text{M}(\text{CH}_2\text{Ph})_2$  via elimination of toluene with sufficiently acidic  $(\text{L}^{\text{FI}})$ -H ligands; however, subsequent intramolecular migration of the metal-bound benzyl group to imine functions was often problematic.<sup>42,100,112,149,151,152</sup> For the synthesis of simple methyl complexes,  $(\text{L}^{\text{FI}})_2\text{TiMe}_2$  or  $(\text{L}^{\text{FI}})_2\text{TiBrMe}$ , Fujita and co-workers employed salt metathesis reactions between  $\text{TiMe}_2\text{Cl}_2$ (dme) or  $\text{TiMeBr}_3$  and  $(\text{L}^{\text{FI}})\text{Na}$ .<sup>153</sup> See also section 3.2.1 for details with regard to the synthesis and activation of group 4 bis(phenoxy-imine) and related complexes.

For the synthesis of monoligated  $(\text{L}^{\text{FI}})\text{MX}_3$  complexes, Ladipo and co-workers reported that  $(\text{L}^{\text{FI}})$ -SiMe<sub>3</sub> and TiCl<sub>4</sub> afforded the desired  $(\text{L}^{\text{FI}})\text{TiCl}_3$  via Me<sub>3</sub>SiCl elimination, while  $(\text{L}^{\text{FI}})$ -H and TiCl<sub>4</sub> gave a mixture of products.<sup>101</sup> Bochmann and co-workers also found that the equimolar reaction with  $(\text{L}^{\text{FI}})\text{Li}$  and TiCl<sub>4</sub> resulted in an intractable mixture, but the reaction with  $(\text{L}^{\text{FI}})$ -SiMe<sub>3</sub> and TiCl<sub>4</sub>(thf)<sub>2</sub> gave pure monoligated complexes.<sup>154,155</sup> Marks and co-workers also employed this method to prepare binuclear phenoxy-imine complexes.<sup>131,133</sup>

**2.2.3. Group 5 Metals.** Floriani and co-workers synthesized and characterized a variety of vanadium based phenoxy-imine complexes. Oxyvanadium(IV) complexes  $(\text{L}^{\text{FI}})_2\text{V}=\text{O}$  or  $(\text{L}^{\text{FI}}-\text{FI})\text{V}=\text{O}$  ( $\text{L}^{\text{FI}}-\text{FI}$ : tetradentate bridged  $[\text{O},\text{N},\text{N},\text{O}]$  phenoxy-imine ligands) were prepared from  $\text{VOSO}_4 \cdot \text{SH}_2\text{O}$  as a metal source in aqueous solution.<sup>237,238</sup> The V(III) chlorides,  $(\text{L}^{\text{FI}}-\text{FI})\text{VCl}(\text{L})$ , were obtained by the reaction of the oxyvanadium complexes,  $(\text{L}^{\text{FI}}-\text{FI})\text{V}=\text{O}$ , and  $\text{TiCl}_3(\text{thf})_3$  via a reductive deoxygenation or rather directly by the reaction of  $\text{VCl}_3(\text{thf})_3$  and sodium salts of the phenoxy-imine ligands in THF.<sup>37,238</sup> Redshaw and co-workers synthesized  $(\text{L}^{\text{FI}}-\text{FI})\text{V}(\text{IV})\text{X}$  (X: O, N-*p*-tolyl) complexes bearing sulfur containing bridging groups from  $[\text{VO(O}^{\text{Pr}})]_3$  or  $[\text{V}(\text{N-}p\text{-tolyl})(\text{OEt})_3]$  as metal sources and neutral ligands,  $(\text{L}^{\text{FI}}-\text{FI})\text{H}_2$ .<sup>239</sup> They also obtained  $(\text{L}^{\text{FI}}-\text{FI})\text{V}(\text{III})\text{Cl}$  from  $[\text{VO(O}^{\text{Pr}})]_3$  in the presence of dimethylaluminum chloride or from  $\text{VCl}_3(\text{thf})_3$ . These alkoxide precursors were used instead of  $\text{VOCl}_3$  in order to avoid the liberation of HCl, which can cause a side reaction, particularly with imido complexes.<sup>189</sup> Mono- or bis(phenoxy-imine) or ( $\beta$ -ketoimine) vanadium chlorides were synthesized from  $\text{VCl}_3(\text{thf})_3$  and neutral ligands in the presence of triethylamine<sup>240–242</sup> or from  $\text{VCl}_3(\text{thf})_3$  and lithium<sup>243</sup> or sodium<sup>98</sup> salts of the ligands. Nomura and co-workers reported on  $(\text{L}^{\text{FI}})\text{V}(\text{arylimido})\text{X}_2$  complexes **26–28** synthesized from (arylimido)vanadium trichloride **25** and  $(\text{L}^{\text{FI}})\text{Li}$  (Scheme 10).<sup>244</sup> Reactions between NbCl<sub>5</sub> or TaCl<sub>5</sub>

Scheme 10

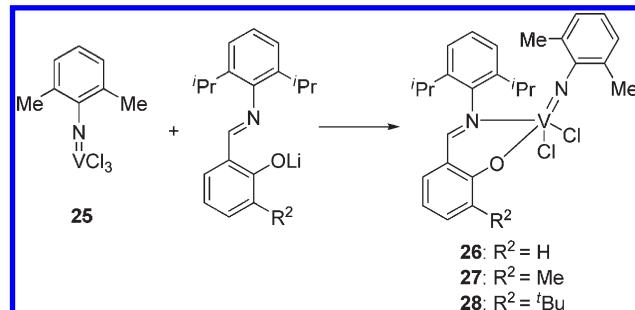
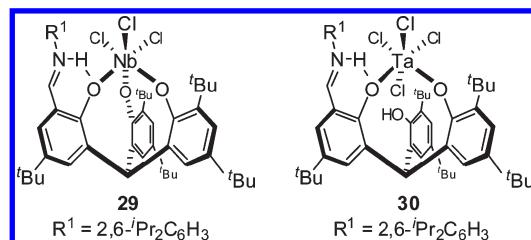
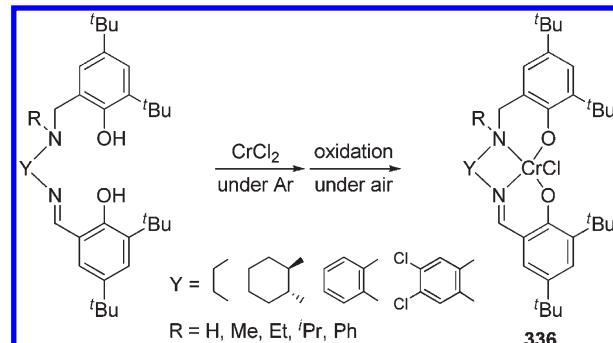


Chart 3



Scheme 11



and triphenol-imine ligands,  $(\text{L}^{\text{FI}})\text{H}_3$ , afforded a Nb diphenolate,  $[(\text{L}^{\text{FI}})-\text{H}]\text{NbCl}_3$  (**29**; Chart 3), and Ta monophenolate,  $[(\text{L}^{\text{FI}})\text{H}_2]\text{TaCl}_4$  (**30**), where the imine groups were involved in intramolecular hydrogen bonding with *ortho*-OH groups and not in the coordination to the metal centers.<sup>189</sup>

**2.2.4. Group 6 Metals.** Gibson and co-workers reported on the synthesis of Cr-based phenoxy-imine complexes,  $(\text{L}^{\text{FI}})_2\text{CrCl}$  (**31** in Scheme 28), via salt metathesis of  $\text{CrCl}_3(\text{thf})_3$  and  $(\text{L}^{\text{FI}})\text{Li}$  prepared from  $(\text{L}^{\text{FI}})$ -H and  $^7\text{BuLi}$ .<sup>245</sup> Later on, they found that  $\text{CrCl}_2(p\text{-tolyl})(\text{thf})_3$  afforded  $(\text{L}^{\text{FI}})\text{CrCl}_2(\text{thf})_n$  in high yield and could be used as a suitable metal source for high throughput screening studies.<sup>88,96,246</sup> The same precursor was employed for the synthesis of *N*-ferrocenyl phenoxy-imine Cr complexes.<sup>192</sup> In addition, Nozaki and co-workers obtained salalen Cr complexes (Scheme 11) from  $\text{CrCl}_2$  and neutral ligands, followed by oxidation with air.<sup>247</sup>

**2.2.5. Group 7–9 Metals.** Apart from commercially available  $\text{Mn}(\text{salen})\text{Cl}$ ,<sup>248</sup> Scott and co-workers prepared tetradentate  $[\text{O},\text{N},\text{N},\text{O}]$  Mn Schiff base complexes,  $(\text{L}^{\text{FI}}-\text{FI})\text{Mn}(\text{II})$  from  $(\text{L}^{\text{FI}}-\text{FI})\text{Na}_2$  and  $\text{MnCl}_2$ .<sup>249</sup>

Scheme 12

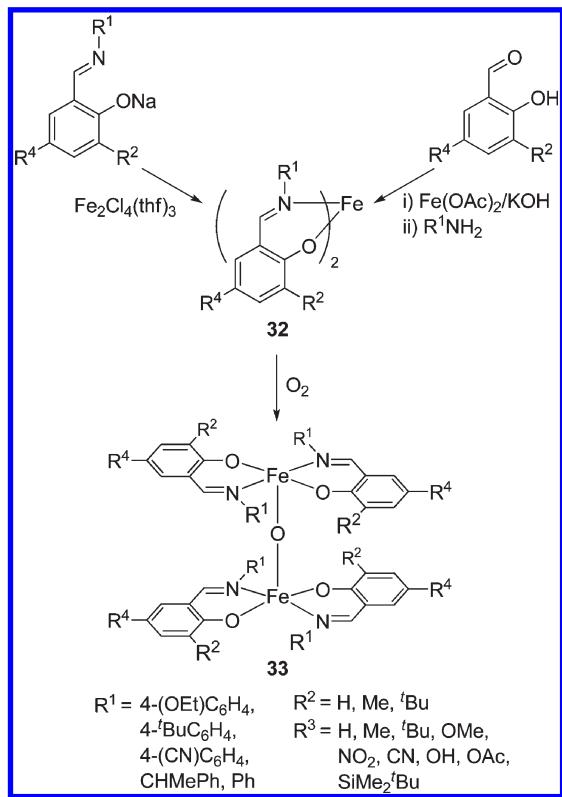
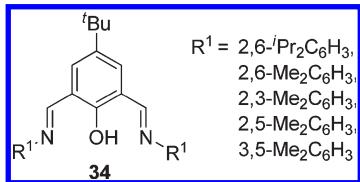


Chart 4



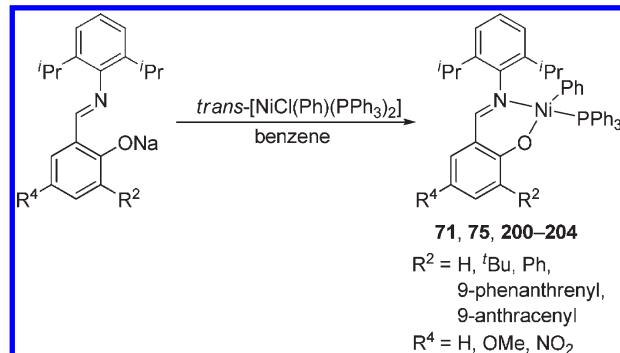
He and co-workers prepared Fe(salphen) or Fe(salen) complexes<sup>250,251</sup> according to the method reported by Marvel et al., i.e., the reactions between (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> and (L<sup>FI</sup>-FI)<sub>2</sub>H<sub>2</sub> in hot H<sub>2</sub>O/methanol.<sup>252</sup> Yasuda and co-workers obtained a [O,N,N] tridentate (L<sup>FI</sup>)<sub>2</sub>FeCl complex by salt metathesis of (L<sup>FI</sup>)Li with FeCl<sub>2</sub> in THF.<sup>97</sup> Lee and co-workers also obtained β-ketoiminato 2:1 complex (L<sup>KI</sup>)<sub>2</sub>Fe from (L<sup>KI</sup>)Li and FeCl<sub>2</sub>.<sup>241</sup> Similarly, (L<sup>FI</sup>)Na and Fe<sub>2</sub>Cl<sub>4</sub>·3THF or (L<sup>FI</sup>)<sub>2</sub>H and Fe(OAc)<sub>2</sub>/KOH/RNH<sub>2</sub> afforded (L<sup>FI</sup>)<sub>2</sub>Fe (32), which was readily oxidized by dry O<sub>2</sub> into μ-oxo complexes (L<sup>FI</sup>)<sub>2</sub>Fe-O-Fe-(L<sup>FI</sup>)<sub>2</sub> (33) (Scheme 12).<sup>253</sup>

Cobalt complexes (L<sup>FI</sup>)<sub>2</sub>Co can be obtained from Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and neutral ligands or from Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, salicylaldehydes, and appropriate amines in one pot.<sup>254–257</sup> Similarly, CoCl<sub>2</sub> afforded bis-ligated complexes (L<sup>KI</sup>)<sub>2</sub>Co with (L<sup>KI</sup>)Li or with (L<sup>KI</sup>)<sub>2</sub>H in the presence of triethylamine,<sup>258,259</sup> while equimolar mixtures of neutral bis(imino)phenoxy ligands 34 (Chart 4) and CoCl<sub>2</sub>·6H<sub>2</sub>O furnished adduct complexes [(L<sup>FI</sup>)<sub>2</sub>H]<sub>2</sub>CoCl<sub>2</sub>.<sup>260–263</sup>

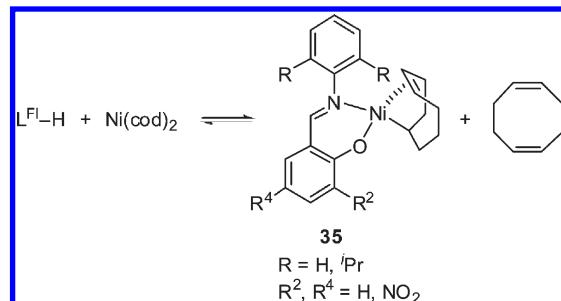
#### 2.2.6. Group 10 Metals

**2.2.6.1. Ni Complexes.** Since Grubbs and co-workers reported that mono(phenoxy-imine) Ni(II) complexes (L<sup>FI</sup>)NiX(L) were obtainable from trans-[NiCl(Ph)(PPh<sub>3</sub>)<sub>2</sub>] and (L<sup>FI</sup>)Na (Scheme 13) when sufficient steric bulk of an R<sup>2</sup> substituent

Scheme 13



Scheme 14



prevented disproportionation,<sup>22,264,265</sup> this and similar synthetic routes have been widely applied to the synthesis of a variety of related Ni complexes.<sup>67,81,82,266–274</sup> They were also applied to the preparation of binuclear Ni complexes<sup>121–123,128,129</sup> and β-ketoimine Ni complexes.<sup>269,275–279</sup> Similar metal sources of the type trans-[NiX(Ar)(PPh<sub>3</sub>)<sub>2</sub>] (X: Cl, Br; Ar: Ph, o-tolyl, p-tolyl, 1-naphthyl, mesityl etc.) were also employed for the synthesis of phenoxy-imine or related Ni complexes.<sup>132,134,280–287</sup> The metal precursors can be reacted with alkali metal salts or with neutral protic ligands in the presence of triethylamine.<sup>123,280–282</sup> Mixtures of mono- and bis-ligated Ni complexes were obtained via the reactions with the metal sources and 2-oxazolylphenol in the presence of triethylamine, while the reaction with the sodium salts gave monoligated complexes.<sup>281,282</sup> For the introduction of alkyl or allyl groups instead of aryl groups described above, trans-[NiMeCl(PMe<sub>3</sub>)<sub>2</sub>],<sup>132,134,288</sup> NiCl(η<sup>3</sup>-CH<sub>2</sub>Ph)-(PMe<sub>3</sub>),<sup>120,135,289,290</sup> [NiCl(η<sup>3</sup>-CH<sub>2</sub>CMeCH<sub>2</sub>)],<sup>291</sup> and [NiCl(η<sup>1</sup>-CH<sub>2</sub>Ph)(PMe<sub>3</sub>)<sub>2</sub>]<sup>292,293</sup> were also employed as metal sources. Carlini and co-workers suggested that the oxidative addition of (L<sup>FI</sup>)<sub>2</sub>H to Ni(cod)<sub>2</sub> yielded alkyl complexes of the type (L<sup>FI</sup>)Ni(η<sup>1</sup>,η<sup>2</sup>-cycloocten-1-yl) (35) based on <sup>1</sup>H NMR and IR spectra of the products (Scheme 14).<sup>294,295</sup>

Due to strongly coordinating phosphine donors, those complexes described above generally require a phosphine scavenger such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Ni(cod)<sub>2</sub>. A metal source, NiMe<sub>2</sub>(tmida) (tmida = N,N,N',N'-tetramethylethylenediamine), provides a facile route to prepare phosphine free complexes via the reactions with (L<sup>FI</sup>)<sub>2</sub>H in the presence of an excess of more labile donors, for example, pyridine,<sup>67,69,70,72,76,296,297</sup> MeCN,<sup>87,296</sup> DMSO,<sup>298</sup> and TMEDA.<sup>299</sup> The NiMe<sub>2</sub>(tmida) precursor was also applied to β-ketoiminato,<sup>300,301</sup> diaza,<sup>302</sup> and binuclear complexes.<sup>75</sup> These complexes having labile donors served as a single component catalyst without the need for a scavenger, showing generally

**Table 2.** Synthetic Methods and Metal Sources for the Synthesis of Bis-ligated Group 10 Metal Phenoxy–Imine and Phenoxy–Imine-Related Complexes

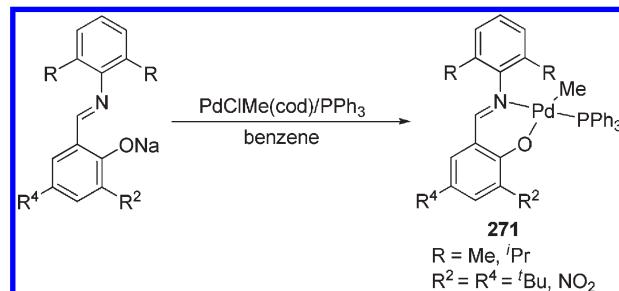
ligand	deprotonation	metal source	product	refs
phenoxy–imine	<sup>a</sup>	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	(L <sup>FI</sup> ) <sub>2</sub> Ni	80, 305–307, 313–315
phenoxy–imine	<sup>a</sup>	NiBr <sub>2</sub> (dme)	(L <sup>FI</sup> ) <sub>2</sub> Ni	312
phenoxy–imine	MeLi	NiBr <sub>2</sub> (dme)	(L <sup>FI</sup> ) <sub>2</sub> Ni	316
phenoxy–imine	NaH	NiCl <sub>2</sub> ·6H <sub>2</sub> O	(L <sup>FI</sup> ) <sub>2</sub> Ni	105, 317, 318
phenoxy–imine	<sup>a</sup>	NiMe <sub>2</sub> (tmeda)	(L <sup>FI</sup> ) <sub>2</sub> Ni	192
phenoxy–imine	NaH	<i>trans</i> –[NiCl(Ph)(PPh <sub>3</sub> ) <sub>2</sub> ]	(L <sup>FI</sup> ) <sub>2</sub> Ni	270
phenoxy–imine	<sup>a</sup>	NiMe <sub>2</sub> (tmeda)	(L <sup>FI</sup> ) <sub>2</sub> Ni(tmeda)	87
phenoxy–imine	(Na)	Ni(cod) <sub>2</sub>	[Ni(L <sup>FI</sup> )OH] <sub>2</sub>	316
phenoxy–imine	DBU	NiBr <sub>2</sub> ·6H <sub>2</sub> O	[Ni(L <sup>FI</sup> )OH] <sub>2</sub>	316
phenoxy–imine	<sup>a</sup>	Ni(acac)	Ni(L <sup>FI</sup> )(acac)	316
phenoxy–imine	MeLi	NiBr <sub>2</sub> (dme)	(L <sup>FI</sup> ) <sub>2</sub> Ni	316
β-ketoimine	<sup>t</sup> BuOK	NiBr <sub>4</sub> (Et <sub>4</sub> N) <sub>2</sub>	(L <sup>KI</sup> ) <sub>2</sub> Ni	319–322
β-ketoimine	<sup>n</sup> BuLi	NiBr <sub>2</sub> (dme)	(L <sup>KI</sup> ) <sub>2</sub> Ni	323–325
β-ketoimine	<sup>a</sup>	NiBr <sub>2</sub>	(L <sup>KI</sup> ) <sub>2</sub> Ni	326
β-ketoimine	NaH	NiBr <sub>2</sub>	(L <sup>KI</sup> ) <sub>2</sub> Ni	326
β-ketoimine	Et <sub>3</sub> N	NiCl <sub>2</sub>	(L <sup>KI</sup> ) <sub>2</sub> Ni	258, 327
phenoxy–imidazol	<sup>n</sup> BuLi	NiCl <sub>2</sub>	(L <sup>IM</sup> ) <sub>2</sub> Ni <sup>b</sup>	328
phenoxy–imidazol	KOH	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	(L <sup>IM</sup> ) <sub>2</sub> Ni	329
indanimine	<sup>a</sup>	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	(L <sup>IN</sup> ) <sub>2</sub> Ni <sup>c</sup>	330, 331
phenoxy–oxazoline	Et <sub>3</sub> N	<i>trans</i> –[NiCl(Ph)(PPh <sub>3</sub> ) <sub>2</sub> ]	(L <sup>FO</sup> ) <sub>2</sub> Ni, (L <sup>FO</sup> )NiPh(PPh <sub>3</sub> ) <sup>d</sup>	281

<sup>a</sup> Metalation was conducted without deprotonating reagents. <sup>b</sup> L<sup>IM</sup>: phenoxy–imidazol ligand. <sup>c</sup> L<sup>IN</sup>: indanimine ligand. <sup>d</sup> L<sup>FO</sup>: phenoxy–oxazoline ligand.

higher activities than those of the corresponding phosphine coordinated complexes.<sup>87,264,298,299</sup> Furthermore, this synthetic approach provides a means to control the solubility and stability of the complexes by selecting or designing appropriate neutral ligands (L). For example, Mecking and co-workers synthesized a series of (L<sup>FI</sup>)NiMe(L), where L was a neutral donor varied in hydrophilicity, such as hexamethylenetetramine (urotropine), tetraethylammonium pyridine-3-sulfonate [tri(sodiumphenylsulfonate)phosphine], [di(sodiumphenylsulfonate)phenylphosphine], or H<sub>2</sub>N–PEG [H<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>Me, n = ca. 52], to control the solubility of the complexes in water.<sup>70,74,303</sup> Similarly, Dahrensbourg and co-workers obtained (L<sup>FI</sup>)NiMe(PTA) (PTA = 1,3,5-triaza-7-phosphaadamantane), although the strong binding of PTA hampered the dissociation even in a toluene/water biphasic system despite the water-soluble nature of PTA.<sup>304</sup> Another metal source, NiMe<sub>2</sub>-(pyridine)<sub>2</sub> instead of NiMe<sub>2</sub>(tmeda) can also be applied with (L<sup>FI</sup>)–H for the synthesis of (L<sup>FI</sup>)NiMe(pyridine).<sup>75,77,78,296</sup>

Bis(phenoxy–imine) Ni complexes, (L<sup>FI</sup>)<sub>2</sub>Ni, were examined as a polymerization catalyst with cocatalysts such as MAO or alkylaluminums. Many of the bis-ligated complexes were synthesized<sup>80,305–308</sup> according to the known literature methods,<sup>309–311</sup> via salt metathesis reactions, which are summarized in Table 2.

Tridentate Ni complexes bearing an 8-quinolinyl group as R<sup>1</sup> substituents were synthesized from NiCl<sub>2</sub>·6H<sub>2</sub>O.<sup>99</sup> Adduct complexes were obtained for neutral bis(imino)phenol and NiBr<sub>2</sub>(dme) or NiCl<sub>2</sub>·6H<sub>2</sub>O,<sup>260,263</sup> but NiBr<sub>2</sub>(dme) and a neutral ligand (R<sup>2</sup> = formyl) afforded a metalated complex, (L<sup>FI</sup>)<sub>2</sub>Ni.<sup>312</sup> Janiak and co-workers reported binuclear Ni complexes synthesized from Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O.<sup>119</sup> Solan and co-workers synthesized binuclear bis(imino-pyridyl)phenoxy Ni complexes from NiBr<sub>2</sub>(dme).<sup>262</sup> Mapolie and co-workers reported dendric bi- or tetranuclear Ni complexes synthesized from

**Scheme 15**

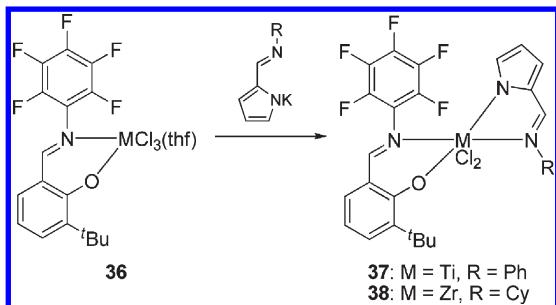
Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O.<sup>124</sup> Shen and co-workers obtained N-heterocyclic carbene Ni complexes via a reaction of NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and a phenoxy–imine ligand possessing imidazolium bromide at R<sup>1</sup> in the presence of 2 equiv of Na(SiMe<sub>3</sub>)<sub>2</sub>.<sup>117</sup>

**2.2.6.2. Pd Complexes.** Palladium complexes bearing a phenoxy–imine or related ligand, (L<sup>FI</sup>)PdMe(PPh<sub>3</sub>), can be synthesized from PdClMe(cod) and (L<sup>FI</sup>)Na in the presence of a donor compound such as Ph<sub>3</sub>P<sup>332</sup> or imines (PhCH=NR) (R = Me, <sup>n</sup>Pr, <sup>t</sup>Bu, Ph, CH<sub>2</sub>Ph)<sup>333</sup> (Scheme 15). Similarly, β-ketoiminato complexes were obtained from PdClMe(cod) and (L<sup>FI</sup>)K.<sup>320,334</sup> Li and co-workers prepared binuclear Pd complexes in a similar way, that is, a reaction with PdClMe(cod) in the presence of PPh<sub>3</sub> or pyridine.<sup>129</sup> A palladium complex having a monoanionic tridentate [O,N,P] ligand, (L<sup>FI</sup>)PdMe, was synthesized from PdClMe(cod) and (L<sup>FI</sup>)–H in the presence of triethylamine.<sup>108</sup> Another tridentate [O,N,N] ligand, (L<sup>FI</sup>)–H, was complexed with PdCl<sub>2</sub> in THF, affording (L<sup>FI</sup>)PdCl.<sup>99</sup> Janiak and co-workers reported on the synthesis of binuclear Pd complexes from PdCl<sub>2</sub>(MeCN)<sub>2</sub>.<sup>119</sup>

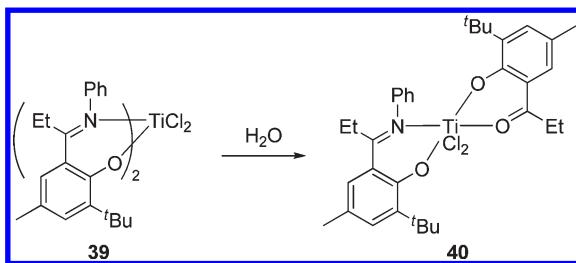
**2.2.7. Group 11–14 Metals.** Carlini and co-workers obtained the  $(L^{FI})_2Cu$  complex via a reaction of  $Cu(OAc)_2$  with  $(L^{FI})-H$  in MeOH.<sup>335,336</sup> Foley and co-workers prepared a dimeric complex  $[(L^{FI})CuCl]_2$  through the reaction of  $CuCl_2$  with the salts,  $(L^{FI})Na$ .<sup>337</sup> Wu and co-workers prepared  $(L^{KI})_2Cu$  from  $Cu(OAc) \cdot 2H_2O$  and  $(L^{KI})-H$ .<sup>338</sup>

Gibson and co-workers synthesized  $(L^{FI})AlMe_2$  complexes with various R<sup>1</sup> substituents (including tridentate ligands having a pendant donor at R<sup>1</sup>) via the complexation of  $(L^{FI})-H$  with

Scheme 16



Scheme 17



trimethylaluminum.<sup>95,118,339,340</sup> Pappalardo and co-workers also reported on a similar method<sup>341</sup> and applied this to the Al complexes bearing 2-anilinotropone ligands.<sup>342</sup> These phenoxy-imine Al complexes can be generated in situ via a ligand transfer reaction when transition metal phenoxy-imine complexes are activated with MAO or other alkylaluminums (see also section 3.2.1).<sup>337</sup>

Pappalardo and co-workers synthesized  $(L^{FI})_2SnR_2$  (R = alkyl) complexes (as a mimic of the group 4 metal complexes) via a salt metathesis reaction of  $(L^{FI})Na$  and the corresponding  $Cl_2SnR_2$  in dry THF.<sup>343,344</sup> These Sn complexes were configurationally fluxional in solution in their neutral states and could be activated by  $[Ph_3C][B(C_6F_5)_4]$  into cationic species, thus exhibiting ethylene oligomerization activities.

**2.2.8. Heteroligated Complexes.** As discussed in section 2.2.2, Ladipo<sup>101</sup> and Bochmann<sup>154,155</sup> reported that the reaction of  $(L^{FI})-SiMe_3$  and  $MCl_4(\text{thf})_2$  (M: Ti, Zr) afforded monoligated phenoxy-imine group 4 metal complexes,  $(L^{FI})MCl_3(\text{thf})$ , which served as a metal source for heteroligated complexes. Coates and co-workers synthesized  $(L^{FI})TiCl_3(\text{thf})$  via reactions of  $(L^{FI})-H$  and  $TiCl_4(\text{thf})_2$  at  $-78^\circ\text{C}$ , and the monoligated complexes were reacted with  $(L^{FI})Li$ , affording heterobis(phenoxy-imine) ligated complexes  $(L^{FI})(L^{FI})TiCl_2$ .<sup>194</sup> Similarly, mixed-ligand complexes having another type of bidentate ligand,  $(L^{FI})(L^X)MCl_2$  (M = Ti, Zr), were synthesized using  $(L^{FI})MCl_3(\text{thf})$  (36) as a metal source with potassium salts of the pyrrolide-imine ligands, giving  $(L^{FI})(\text{pyrrolide-imine})MCl_2$  (37, 38; M = Ti, Zr) (Scheme 16),<sup>308,345,346</sup> and with potassium salts of  $\beta$ -ketoinime ligands, affording  $(L^{FI})(L^{KI})TiCl_2$ .<sup>347,348</sup> Fujita and co-workers reported that phenoxy-ketimine and phenoxy-ketone heteroligated titanium complex 40 could be obtained by the slow hydrolysis of the bis(phenoxy-ketimine) complex 39 (Scheme 17).<sup>349</sup>

Hybrid complexes having a phenoxy-imine ligand and a cyclopentadienyl ligand can be synthesized using monocyclopentadienyl

Table 3. Synthetic Methods and Metal Sources for the Synthesis of Phenoxy-Imine/Cyclopentadienyl Hybrid Complexes

ligand	deprotonation	metal source	product	ref
phenoxy-imine	"BuLi	$CpTiCl_3$	$(Cp)(L^{FI})_2TiCl$ , $(Cp)(L^{FI})TiCl_2$ , $(Cp)(L^{FI})TiCl$	104
phenoxy-imine	"BuLi	$CpTiCl_3$ , $CpZrCl_3(\text{dme})$	$(Cp)(L^{FI})MCl_2$ (M = Ti, Zr)	190
phenoxy-imine	Et <sub>3</sub> N	$CpZrCl_3(\text{dme})$	$(Cp)(L^{FI-FI})ZrCl$	350
phenoxy-imine	"BuLi	$CpZrCl_3(\text{dme})$	$(Cp)(L^{FI})MCl_2$ , $(Cp)(L^{FI})MCl(\text{thf})$	102, 106
phenoxy-imine	"BuLi	$CpTiCl_3$	$(Cp)(L^{FI})MCl_2$	208
phenoxy-imine	"BuLi	$CpZrCl_3$	$(Cp)(L^{FI})ZrCl_2(\text{thf})$ , $(Cp)(L^{FI})_2ZrCl$	208
phenoxy-imine	"BuLi	$(RCp)ZrCl_3(\text{dme})$	$(RCp)(L^{FI})ZrCl_2$ R = H, Me, <sup>t</sup> Bu	106
phenoxy-imine	"BuLi	$[Cp^*CrCl_2]_2$	$(Cp^*)(L^{FI})CrCl$	351
phenoxy-imine	NaH	$CpMCl_3$ (M = Ti, Zr),	$(Cp)(L^{FI})MCl$	103
phenoxy-imine	"BuLi	$Cp'TiCl_3$	$(Cp')(L^{FI})TiCl$	352
$\beta$ -ketoinime	"BuLi	$Cp''ZrCl_3$	$(Cp^*)(L^{KI})_2ZrCl_2^b$	233
anilinotropone	"BuLi	$CpTiCl_3$	$(Cp)(L^{AT})TiCl_2^c$	353
phenoxy-oxazoline	<sup>a</sup>	$Cp^*MMe_3$ (M = Zr, Hf)	$(Cp^*)(L^{FO})MMe_2$	354
phenoxy-oxazoline	NaH	$CpTiCl_3$	$(Cp)(L^{FO})TiCl_2$	354
phenoxy-oxazoline	NaH	$Cp^*MCl_3$ (M = Zr, Hf)	$(Cp^*)(L^{FO})MCl_2$	354, 355
phenoxy-oxazoline	<sup>a</sup>	$Cp^*TiMe_3$	$(Cp^*)(L^{FO})MMe_2$	355
phenoxy-oxazoline	NaH	$Cp^*TiCl_2Me$	$(Cp^*)(L^{FO})MCl_2$	355
phenoxy-oxazoline	<sup>a</sup>	$Cp^*Zr(NMe_2)3$	$(Cp^*)(L^{FO})Zr(NMe_2)_2$	356
hydroxyindanimine	NaH	$Cp^*CrCl_2$	$(Cp^*)(L^{HI})CrCl^d$	357

<sup>a</sup> Metalation was conducted without deprotonating reagents. <sup>b</sup> L<sup>KI</sup>:  $\beta$ -ketoinato ligand. <sup>c</sup> L<sup>AT</sup>: anilinotropone ligand. <sup>d</sup> L<sup>HI</sup>: hydroxyindanimine ligand.

complexes,  $\text{Cp}'\text{MX}_3$ , and alkali metal salts of phenoxy-imine ligand precursors or related compounds. Examples were summarized in Table 3.

### 3. STRUCTURES AND REACTIONS OF PHENOXY-IMINE COMPLEXES

The primary focus of this section is on what makes phenoxy-imine complexes highly active for an olefin insertion reaction. The polymerization activity in the literature was usually stated in g-polymer/(mmol-M·h·bar), which actually cannot be directly correlated with the kinetic rate constant ( $k_p$ ) of the olefin insertion. The apparent catalytic activity is really a composite of several factors, such as activation (initiation) efficiency and catalyst lifetime. Ideally speaking, the estimation of activities should be made in a regime where nearly quantitative initiation and time independent activity profiles are assured, which is often difficult to achieve. Therefore, the discussion of polymerization activities in this section remains qualitative, and an activity scale for the qualitative comparison is set as follows: very low (<10 g-polymer/(mmol-M·h·bar)); low (10–100 g-polymer/(mmol-M·h·bar)); moderate (100–1000 g-polymer/(mmol-M·h·bar)); high (1–10 kg-polymer/(mmol-M·h·bar)); very high (10–100 kg-polymer/(mmol-M·h·bar)); extremely high (>100 kg-polymer/(mmol-M·h·bar)).

Chain transfer reactions and regio- and stereospecificity, both of which are not directly connected to the activity, will be discussed in the later sections with the specific polymerization characteristics of each complex.

It would be appropriate to focus on group 4 metal bis(phenoxy-imine) complexes (FI catalysts) and Ni mono(phenoxy-imine) complexes, as they have been the most extensively investigated, so that other related catalysts will be discussed relative to these two catalyst systems.

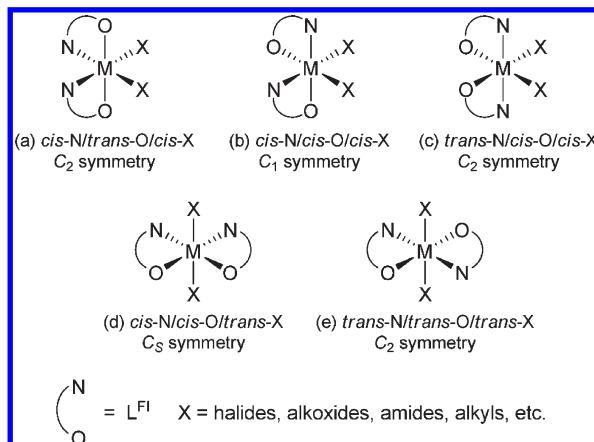
#### 3.1. Geometry

**3.1.1. Geometry of Group 4 Metal Bis(phenoxy-imine) Complexes.** In a tetrahedral framework of group 4 metallocenes,  $\text{Cp}'_2\text{MX}_2$  ( $\text{Cp}'$ : cyclopentadienyl or its substituted derivatives), two nonspectator ligands (X) such as halogens and alkyls, are restricted to be *cis* to each other, which is a prerequisite for efficient insertion or  $\sigma$ -bond metathesis reactions between the M–R bond (R: alkyl, aryl) and the coordinating substrate.<sup>7–11,358</sup>

On the other hand, bis(phenoxy-imine) group 4 metal complexes have an octahedral geometry around the metal (M), furnished with two imine nitrogens, two phenolic oxygens, and two X ligands. There are theoretically five structural isomers for this octahedron, depending on the arrangements of these donor atoms. Note that three of the hypothetical isomers have two X ligands *cis* to each other, and the other two possess *trans*-X geometry (Chart 5). Bis(phenoxy-imine) group 4 metal complexes seem to have an intrinsic tendency to take those *cis*-X geometries due to the substituents on the imine nitrogen ( $R^1$ ) and those adjacent to the phenolic oxygen ( $R^2$ ) of the two phenoxy-imine ligands. These substituents effectively prevent the  $\text{N}_2\text{O}_2$  donors from taking a planar configuration, which is required for the *trans*-X geometry. It should be noted that the classical salen or salphen ligands with group 4 metals are prone to form a stable  $[\text{O},\text{N},\text{N},\text{O}]$  plane with *trans*-oriented X ligands and that these complexes show little activity for ethylene polymerization.<sup>193,209,224,359–361</sup>

In the *cis*-X framework of bis(phenoxy-imine) group 4 metal complexes, the rest of the donors are most often found to have a

Chart 5



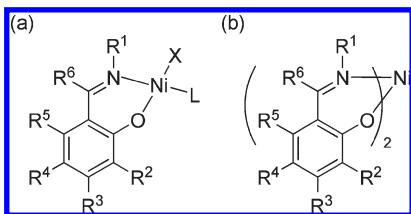
*cis*-N/*trans*-O geometry (Chart 5a) in the solid state, in solution, and in computed structures, probably because M–O bonds are significantly shorter than M–N bonds. However, when  $R^1$  is sterically demanding (for example, tertiary alkyls), *trans*-N/*cis*-O/*cis*-X isomers (Chart 5c) seem to be preferred.<sup>144,362,363</sup> A fraction of *cis*-N/*cis*-O/*cis*-X isomers (Chart 5b) are sometimes observed in solution with major *cis*-N/*trans*-O/*cis*-X isomers<sup>162,216,218</sup> and isolated in one case as a single crystal.<sup>148</sup> The reason why some complexes tend to hold this *cis*-N/*cis*-O/*cis*-X geometry is not clear, but the substituent para to the phenolic oxygen ( $R^4$ ) may be involved in their preference for this particular geometry.

These isomers are often in a dynamic equilibrium in solution, and exchange between isomers was observed by  $^1\text{H}$  NMR.<sup>142,144,148,216,236</sup> The isomerization was proposed to take place via the dissociation of a labile M–N bond.<sup>39,363,364</sup> Multisite characters of some bis(phenoxy-imine) group 4 metal complexes are considered to be caused by the multiple isomers as a result of the isomerization<sup>26,188,216,218</sup> or by the interaction of heteroatoms with cocatalysts when  $R^4 = \text{MeO}$ .<sup>91</sup>

As mentioned above, tetradentate salen and its derivatives generally result in complexes with *trans*-X geometry. However, there are examples of tetradentate Schiff base complexes, where the modified bridging parts between the imine nitrogens make the X ligands prone to *cis*-orientation, which will be discussed in section 6.1 in more detail but is briefly mentioned here. Tetradentate bis(phenoxy-imine) ligands possessing a 2,2'-biaryl bridge<sup>41,43,149,151,152,226,227,229</sup> or bis(phenoxy-ketimine) ligands having a *trans*-1,2-cyclohexylene bridge afforded complexes with a *cis*-Cl geometry about the metal center.<sup>40,42</sup> These complexes catalyzed ethylene polymerization with MAO, albeit low in activity.

Despite the apparent similarity of these tetradentate bridged bis(phenoxy-imine) and nonbridged bis(phenoxy-imine) complexes, both of which have *cis*-oriented X ligands with *cis*-N/*trans*-O geometry, the bridged complexes exhibited far lower activities for ethylene polymerization. This can stem from the significant constraints imposed by the rigid structures in turn imposed by the relatively short linkage.<sup>42,152</sup> Interestingly, when the bridge parts between the imine nitrogens are extended to the  $\text{C}_6$ -linkage, much higher activity was observed by Fujita<sup>210</sup> and Gibson<sup>193</sup> and their co-workers, which may imply that the flexibility of the ligand coordination is important for high activity.

Chart 6



The dynamic and flexible nature of two nonbridged phenoxy-imine ligands, contrary to a stereorigid but otherwise electrostatically nearly equivalent tetradentate bis(phenoxy-imine) ligand, can be the reason for the exceptionally high activity of bis(phenoxy-imine) group 4 metal complexes.<sup>24,205</sup>

Mono(phenoxy-imine) group 4 metal complexes of the type ( $L^{FI}$ )MCl<sub>3</sub>(L) were also prepared.<sup>131,133,138,154,155</sup> Bulky R<sup>1</sup> (for example, 2,6-disubstituted phenyl) and/or an extra donor (L) are usually required to avoid the formation of bis-ligated ( $L^{FI}$ )<sub>2</sub>MCl<sub>2</sub> complexes. However, these ( $L^{FI}$ )MCl<sub>3</sub>(L) showed very low to moderate activity for ethylene polymerization. Disproportionation of ( $L^{FI}$ )MCl<sub>3</sub>(L) to ( $L^{FI}$ )<sub>2</sub>MCl<sub>2</sub> was proposed in order to explain the observed multisite behavior.<sup>155</sup> Attempts to improve the catalytic performance of mono(phenoxy-imine) complexes were made by using tridentate phenoxy-imine ligands that have a pendant donor at the R<sup>1</sup> group, and this will be discussed in section 5.

**3.1.2. Geometry of Phenoxy-Imine Ni Complexes.** Mono(phenoxy-imine) Ni(II) complexes usually have a square planar geometry bearing a phenoxy-imine ligand, an anionic ligand (X), and a neutral donor (L), ( $L^{FI}$ )MX(L) as shown in Chart 6a. The X and L ligands are usually situated trans to phenolic oxygen and imine nitrogen, respectively, and therefore, the polymerization site becomes nonsymmetric to the Ni-C bond and coordinating olefin during olefin insertion polymerization. When the R<sup>2</sup> is not sufficiently large, bis-ligation of  $L^{FI}$  affords a complex of the type ( $L^{FI}$ )<sub>2</sub>Ni (Chart 6b) (for example, ref 87). When the R<sup>2</sup> is large (9-anthracyl) but the R<sup>1</sup> is relatively small (phenyl), octahedral ( $L^{FI}$ )<sub>2</sub>Ni(tmeda) was also isolated in the phosphine free synthesis using [NiMe<sub>2</sub>(tmeda)].<sup>87</sup> These bis-ligated complexes are essentially inactive toward olefin polymerization.

The bulky R<sup>1</sup> (2,6-disubstituted phenyl groups are commonly employed) is also necessary to obtain high molecular weight polymers by blocking the axial faces of the Ni center, which is considered to discourage chain transfer reaction to the coordinating monomer in an associative manner, as suggested for Brookhart's diimine Ni and Pd complexes.<sup>16</sup>

### 3.2. Activation and Active Species

Most of the olefin polymerization catalysts need to be activated with cocatalysts in order to really function as a catalyst for olefin polymerization (in this sense, they are actually catalyst precursors before activation, but in this article, both terms, catalyst and precursor, will be used without causing misunderstanding). In general, alkylaluminums such as R<sub>3</sub>Al and R<sub>3-n</sub>AlCl<sub>n</sub> ( $n = 1, 2$ ) have been employed as cocatalysts for classical titanium Ziegler-type catalysts. Thus, the activation of catalyst precursors by cocatalysts has been considered to include one or both of the following: (1) alkylation of M-X bonds in the precursor, making at least one M-R bond, and (2) development of coordinative and electronic unsaturation at the metal center.

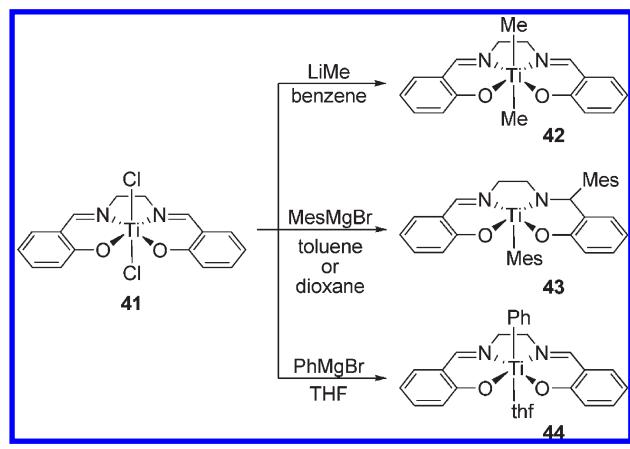
However, these activation processes and the resulting active species have not been well characterized due to the heterogeneous and nonuniform nature of the catalysts.<sup>32</sup>

In 1980, Sinn and Kaminsky found that MAO, oligomeric compounds consisting of  $-Al(Me)-O-$  units afforded highly active olefin polymerization catalysts when combined with group 4 metallocenes, which are soluble in organic solvents and chemically homogeneous (single site catalysts).<sup>7–11,358</sup> Generation of a cationic species upon activation was suggested and later unambiguously demonstrated using perfluoroaryl boranes and borates such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [A<sup>+</sup>]B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (A: Ph<sub>3</sub>C, PhNMe<sub>2</sub>H, etc.) as cocatalysts.<sup>365</sup> Those boron-based cocatalysts can stoichiometrically activate metallocene precursors (B/M  $\sim 1$  instead of Al/M = 10<sup>2</sup>–10<sup>3</sup> typical for MAO), resulting in well-defined catalytically active ion pairs, which provide tractable models of active propagating species (contrary to ill-defined MAO) and can also serve as important industrial catalyst systems side by side with MAO. However, it should be noted that, while MAO performs the two functions described above simultaneously (alkylation and generation of unsaturation), the perfluoroaryl boranes and borates have no ability for alkylation of the M-X bonds, and therefore, metallocene alkyls must be prepared beforehand. Alkylation of metallocene halides can be achieved using common alkylating agents such as RLi, RMgX, R<sub>3</sub>Al, and R<sub>2</sub>Zn, for example. Thus, the activation process and the nature of the resulting ion pairs have been extensively studied using metallocene dialkyls and various boron-based cocatalysts. Moreover, the principle and the catalyst design to generate the cationic species are proved to have extensive application generality and they have been successfully applied to many other non-metallocene systems based on early and late transition metals.<sup>17</sup>

On the other hand, mono(phenoxy-imine) Ni(II) complexes, ( $L^{FI}$ )NiX(L), are neutrally charged in their activated form. Therefore, activation requires dissociation of the coordinating neutral ligand (L), which allows the coordination of olefins. For this purpose, Ni(cod)<sub>2</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> are often used for activation. The L dissociation process was also affected by the steric bulkiness of the  $L^{FI}$  ligand substituents, the nature (lability) of L and the polymerization media (solvents or comonomers), polymerization temperature, and so forth, and under appropriate conditions, the complexes can be single component catalysts that require no activating agents.

**3.2.1. Activation and Active Species of Bis(phenoxy-imine) Group 4 Metal Complexes.** For the aforementioned reasons, the activated form of bis(phenoxy-imine) group 4 metal complexes was presumed to be a cationic alkyl species, [( $L^{FI}$ )<sub>2</sub>M-R]<sup>+</sup>. The presumption was indeed supported by several NMR studies on the activation of catalyst precursors with MAO.<sup>366–368</sup> However, alkylation of ( $L^{FI}$ )<sub>2</sub>MX<sub>2</sub> to prepare dialkyl precursors, ( $L^{FI}$ )<sub>2</sub>MR<sub>2</sub>, is not straightforward due to the reactive imine groups in the ligands. The alkylating agents, M'-R (M': Li, Mg, Al, Zn, etc.) are nucleophiles, which of course react with electrophiles, in this case, either the metal center (M) or comparably electrophilic imine carbons (CH=NR<sup>1</sup>). In addition, even though once the alkylated M-R bond is formed, it can subsequently migrate to the imine via intramolecular insertion to form an M-N-CH-R moiety, which is common chemistry for early metals. This tendency is especially salient when M is a highly electrophilic early transition metal in a high oxidation state, which makes the imine even more electrophilic. Therefore, the examples of early metal Schiff base alkyl complexes are rather rare, and alkyl complexes, ( $L^{FI}$ )<sub>2</sub>MR<sub>2</sub>, have not been prepared until recently

Scheme 18



despite many attempts. We describe hereafter an overview of the group 4 metal Schiff base alkyl complexes.

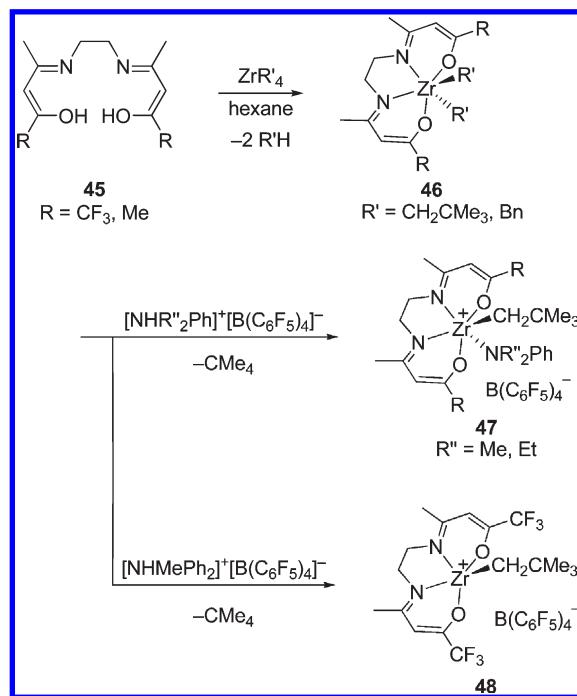
Floriani prepared Ti(salen)Me<sub>2</sub> (**42**) by alkylation of Ti(salen)Cl<sub>2</sub> (**41**) with MeLi under carefully controlled conditions (Scheme 18).<sup>360,369</sup> The dimethyl complex **42** was unstable and decomposed via intramolecular methyl migration to the imine. Other attempted alkylations with various alkylating agents were accompanied by side reactions such as the alkylation of the imines either directly by the alkylating agents or by the M–R migration, resulting in monoalkyl Ti complex **43**, and also the reduction to Ti(III) to form Ti(salen)R(thf) (**44**) in the reactions in THF. As such, the outcomes of the reactions were found to be extremely sensitive to the nature of solvents and alkylating agents.

In 1995, Jordan applied alkane elimination reactions to prepare Zr(IV) alkyl complexes bearing acen and hexafluorinated acen ligands (Scheme 19).<sup>179</sup> The reactions of ZrR'<sub>4</sub> (R': CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>Ph) and R-acen-H<sub>2</sub> (**45**) afforded Zr(R-acen)R'<sub>2</sub> (**46**) in good yields. These dialkyl complexes can be activated by [NHR''<sub>2</sub>Ph]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> to cationic species **47** or base-free species **48**. These dialkyls or base adducts of the cationic species have distorted octahedral geometry, of which the C–Zr–C (or C–Zr–NR''<sub>2</sub>Ph) angles are 130–145°, i.e., between cis- and trans-geometry. The cationic species are active toward insertion chemistry of CO or Ph<sub>2</sub>CO but inactive for the insertion of ethylene. Upon addition of 1 or 2 equiv of AlR<sub>3</sub>, however, they showed low ethylene polymerization activity (14 g-polymer/(mmol·M·h·bar)).<sup>232,370</sup>

Floriani also used the alkane elimination protocol on phenoxy–oxazoline ligands (L<sup>FO</sup>) and successfully obtained alkyl complexes, (L<sup>FO</sup>)<sub>2</sub>M(CH<sub>2</sub>Ph)<sub>2</sub> (**1**, **49**; Scheme 1), which have C<sub>2</sub> symmetric *cis*-N/*trans*-O/*cis*-C geometry.<sup>38</sup> Activation with [HNR<sub>2</sub>Ph][BPh<sub>4</sub>] (R: Me, Et, Bu) or Cp<sub>2</sub>FeBPh<sub>4</sub> of the dialkyl complexes gave the species (L<sup>FO</sup>)<sub>2</sub>M(CH<sub>2</sub>Ph)(thf)/BPh<sub>4</sub> (**2**), where the benzyl group and the coordinating THF are *cis* to each other. The reactions carried out in toluene afforded the species that are active for ethylene polymerization, albeit at a very low rate.

Jordan focused on 8-quinolinol derivatives (L<sup>Ox</sup>–H) as a bidentate ligand and successfully obtained dialkyl complexes, (L<sup>Ox</sup>)<sub>2</sub>MR<sub>2</sub> (M: Zr, Hf; R: CH<sub>2</sub>Ph, CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>), via alkane elimination reactions in 1997 (Scheme 2).<sup>39</sup> It was revealed by NMR studies that these complexes and their

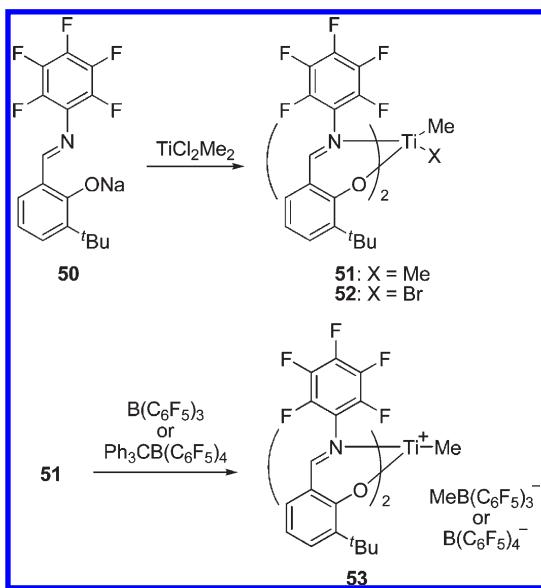
Scheme 19



corresponding cationic complexes possessed *cis*-N/*trans*-O/*cis*-R(L) geometry and underwent Δ/Λ racemization in solution (ΔG<sup>‡</sup>: neutral complexes 15–18 kcal/mol, cationic complexes >20 kcal/mol), suggesting the fluxional character of these complexes. Upon heating, facile benzyl migration to the C<sub>2</sub>-position of 8-quinolinolato (ortho to the nitrogen) was observed. Base-free cationic complexes were obtained, in which the benzyl group coordinated to the metal via a  $\eta^2$ -fashion. Among these cationic complexes, only those which have two bromines at the 5- and 7-positions of 8-quinolinolato showed ethylene polymerization activity up to 41 g-polymer/(mmol·M·h·bar).

Scott and co-workers demonstrated in a series of studies since 1996 that biaryl-bridged tetradentate [O,N,N,O] Schiff base ligands [ $L^{FI-FI}$ ]<sup>2-</sup> afforded ( $L^{FI-FI}$ )MX<sub>2</sub>, where two X ligands were *cis*-oriented (Cl–Zr–Cl = 103.6° is a typical example) and the overall geometry was C<sub>2</sub> symmetric.<sup>41,151,152,226,227</sup> The alkyl complexes obtained via alkane elimination were unstable due to the diastereoselective 1,2-migratory insertion of the M–R to the imine or alkyl migration via a radical pathway in particular instances. Attempts to generate corresponding cationic species were made in 2005 using ( $L^{FI-FI}$ )Zr(CH<sub>2</sub>Ph)<sub>2</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub> at –80 °C.<sup>152</sup> The new species or assumed cationic species were observed with concurrent formation of PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, but they were extremely unstable and decomposed above –30 °C. For comparison, the benzyl complexes of the type ( $L^{FI}$ )<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub> were also obtained by alkane elimination in NMR tube scale reactions as analytically pure compounds. When R<sup>2</sup> = Me, Δ/Λ racemization was observed on an NMR time scale, while the complexes with R<sup>2</sup> = <sup>t</sup>Bu were configurationally stable, suggesting an N-dissociation mechanism for the racemization. Attempts to generate cationic species by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> gave similar results to those for the biaryl-bridged complexes described above. It was also demonstrated that, despite the apparent similarity of their functionality, the 2,2'-biaryldiimino bridged and non-bridged arylimino complexes have significant differences in

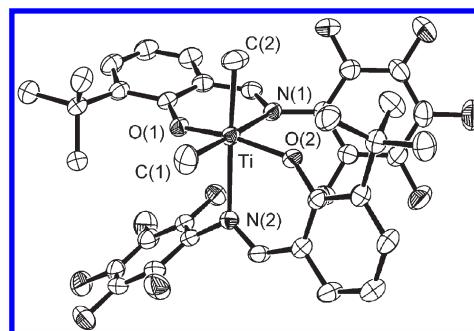
Scheme 20



geometrical parameters, which cause the differences in the olefin polymerization activity and the stability toward 1,2-migratory insertion.

So far, the alkane elimination reaction has been nearly the sole method to achieve group 4 (Schiff base)MR<sub>2</sub> complexes. However, the alkane elimination has drawbacks in that it is applicable only to significantly bulky alkyl groups such as CH<sub>2</sub>Ph, CH<sub>2</sub>CMe<sub>3</sub>, and CH<sub>2</sub>SiMe<sub>3</sub>. These bulky alkyl groups may change the inherent reactivity and structures of the alkyl complexes, and thus, the complexes could be unrealistic models for an olefin polymerization catalyst. The tendency of metal benzyl species (MCH<sub>2</sub>Ph) to afford various multihapto organometallic species is typical of this problem.

Fujita and his co-workers addressed a solution to this problem in 2005. The dimethyl or monomethyl halide group 4 metal complexes, (L<sup>FI</sup>)<sub>2</sub>TiMe<sub>2</sub> (**51**) or (L<sup>FI</sup>)<sub>2</sub>TiMeBr (**52**), are achievable via salt elimination between X<sub>n</sub>MR<sub>4-n</sub> (R: Me; X: Br, Cl; n = 2, 3) and sodium salts of the phenoxy-imine ligands (L<sup>FI</sup>)<sup>-</sup>Na (**50**) (Scheme 20).<sup>153</sup> It is rather surprising that these syntheses were carried out with the worst possible combinations; that is, the complexes have extremely electrophilic C<sub>6</sub>F<sub>5</sub>N=CH groups as the imine moiety and easily reducible Ti(IV) as a metal center. The dimethyl complex **51** exhibited one set of ligand signals in solution, corroborating with the crystallographically determined C<sub>2</sub> symmetric *cis*-N/*trans*-O/*cis*-Me structure (Figure 3). The dimethyl complex **51** can be stoichiometrically and cleanly activated by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> into (L<sup>FI</sup>)<sub>2</sub>TiMe<sup>+</sup>/RB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> (R: Me or C<sub>6</sub>F<sub>5</sub>) (**53**), as expected, without interferences of large MAO signals or complications arising from complex equilibrium with R<sub>3</sub>Al species. The generated species showed comparable activity to MAO-activated species toward olefin polymerization. It was also suggested that the cationic methyl species **53** and the neutral precursors **51** and **52** can form dinuclear cationic complexes [(L<sup>FI</sup>)<sub>2</sub>TiMe(μ-X)Me(L<sup>FI</sup>)<sub>2</sub>Ti]<sup>+</sup>/B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> as a dormant species. The dinuclear and mono-nuclear complexes appear to be in fast equilibrium on an NMR time scale.<sup>371</sup> The mononuclear ion pairs **53** are precipitated out from toluene, implying significant cation-anion separation (outer sphere ion pairs, OSIPs), irrespective of the applied



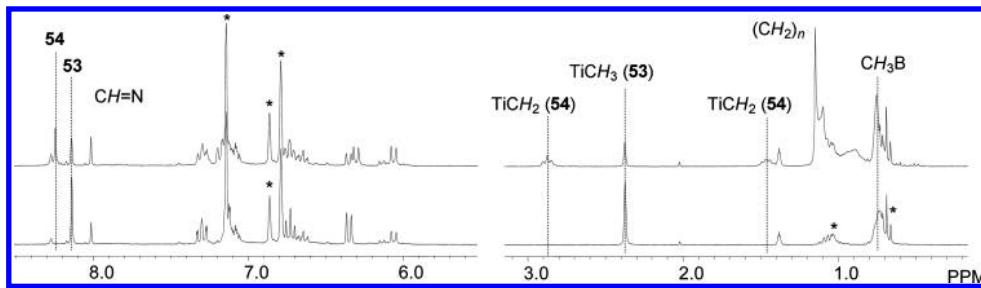
**Figure 3.** Molecular structure of phenoxy-imine Ti dimethyl complex **51**. Selected bond lengths (Å) and bond angles (deg): Ti—O(1), 1.869(2); Ti—O(2), 1.872(2); Ti—N(1), 2.345(3); Ti—N(2), 2.371(3); Ti—C(1), 2.111(4); Ti—C(1), 2.102(4); O(1)—Ti—O(2), 160.3(1); N(1)—Ti—N(2), 93.9(1); C(1)—Ti—C(2), 93.9(2). Reproduced with permission from ref 153. Copyright 2005 The Chemical Society of Japan.

variants in, for example, solvents (toluene, bromobenzene), the size of R<sup>2</sup> (<sup>t</sup>Bu, H), counteranions (MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>), and Ti-bound alkyls (methyl, polymethyl). Therefore, the observed strong ionic characteristics appeared to be the inherent nature of this class of complexes.

The reason why these particular methyl complexes were targeted is that they are known to be extremely active and robust living polymerization catalysts for ethylene and propylene<sup>24,45,372,373</sup> and, therefore, are expected to be “living” for a measurable period after activation and during propagation (see section 4.1). Indeed, those cationic methyl species are stable at ambient temperatures, and moreover, upon addition of a small amount of ethylene (5 equiv to Ti) to [(L<sup>FI</sup>)<sub>2</sub>TiMe]<sup>+</sup>/[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> (**53**), the signals for the methyl cationic species disappeared and those for the new species appeared simultaneously. The most characteristic features of the new species were that two multiplet signals appeared at 1.45 and 2.88 ppm in nearly equal intensity, which are assignable to the diastereotopic α-methylene protons of the propagating species, [(L<sup>FI</sup>)<sub>2</sub>TiCH<sub>2</sub>-polyethylene-Me]<sup>+</sup>/[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> (**54**) (Figure 4).

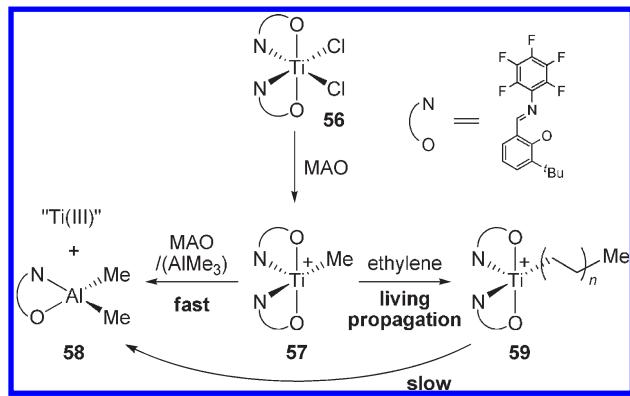
In 2007, Repo reported on the synthesis of (L<sup>FI</sup>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (**55**) via alkyl elimination.<sup>236</sup> The stability of Hf—C bonds relative to the other group 4 metals allowed the isolation of single crystals of the dibenzyl Hf complexes. The solid state structures of the complexes show a distorted octahedral geometry of the C<sub>2</sub> symmetric *cis*-N/*trans*-O/*cis*-C arrangement, which was maintained also in solution (confirmed by 2D-NMR), and the Δ/Λ racemization was slow on the NMR time scale. These Hf dibenzyl complexes can be activated by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> into the corresponding cationic species, [(L<sup>FI</sup>)<sub>2</sub>Hf(η<sup>2</sup>-CH<sub>2</sub>Ph)]<sup>+</sup>/[PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>.<sup>19</sup>F NMR confirmed the OSIPs nature of the species, and 2D-NMR indicated spatial proximity of the R<sup>2</sup> (= <sup>t</sup>Bu) and the methylene and *ortho*-H of the Hf-bound benzyl group, implying a *cis*-N/*trans*-O-like geometry in solution. The broad singlet for the Hf-bound methylene protons at 30 °C was decalesced into an AB doublet at lower temperatures, which is attributable to rapid racemization between Δ/Λ complexes at ambient temperatures ( $ΔG^\ddagger = 10\text{--}14 \text{ kcal/mol}$ ).

While the synthesis of dialkyl complexes was suffering from various side reactions, attempts to see the active species in group 4 metal Schiff base halides activated with MAO have been made simultaneously, which has provided some useful information.



**Figure 4.**  $^1\text{H}$  NMR spectra (270 MHz;  $\text{BrC}_6\text{D}_5$ ) of  $[(\text{L}^{\text{FI}})_2\text{TiMe}]^+/\text{[MeB}(\text{C}_6\text{F}_5)_3]^-(53$ , bottom) and  $[(\text{L}^{\text{FI}})_2\text{TiCH}_2\text{-polyethylene-Me}]^+/\text{[MeB}(\text{C}_6\text{F}_5)_3]^-(54$ , top). The asterisks indicate the protio impurities of NMR solvent and pentane. Reproduced with permission from ref 153. Copyright 2005 The Chemical Society of Japan.

Scheme 21



In 1997, attempts to observe the activation process of  $(\text{salen})\text{ZrCl}_2/\text{MAO}$  ( $\text{Zr}/\text{Al} = 1/20$ ) by  $^1\text{H}$  NMR were made by Repo et al.<sup>361</sup> Due to the low solubility of  $(\text{salen})\text{ZrCl}_2$  in toluene, direct comparison between  $(\text{salen})\text{ZrCl}_2$  and  $(\text{salen})\text{ZrCl}_2/\text{MAO}$  could not be made and the obtained spectra could not be clearly translated.

In 2004, Makio and Fujita demonstrated that the product of  $(\text{L}^{\text{FI}})_2\text{MX}_2/\text{MAO}$  was indeed the assumed cationic methyl species,  $(\text{L}^{\text{FI}})_2\text{M}-\text{Me}^+$ , as a result of NMR experiments using a living bis(phenoxy-imine) Ti complex **56** (Scheme 21).<sup>366</sup> The  $^1\text{H}$  NMR of the reaction mixtures clearly showed the titanium-bound methyl group at 1.97 ppm as a somewhat broad singlet. Due to the robust livingness of this species as mentioned above, the spectra were unusually clean for this kind of experiment. The imine and aromatic protons of the electrophilic cationic methyl species were significantly downfield-shifted relative to the neutral precursor. It was also shown that the cationic methyl species possesses  $C_2$ -symmetry on an NMR time scale. The species,  $[(\text{L}^{\text{FI}})_2\text{M}-\text{Me}]^+/\text{[MAO]}^-$  (**57**), were later shown to be almost identical to the well-defined species **53** generated from the dimethyl complex **51** and  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  (vide supra). In MAO activation, it was found that one of the ligands of  $[(\text{L}^{\text{FI}})_2\text{M}-\text{Me}]^+$  was transferred to  $\text{AlMe}_3$  (included in MAO) and formed  $(\text{L}^{\text{FI}})\text{AlMe}_2$  (**58**) with the liberation of methane, leaving a presumably paramagnetic (NMR silent) Ti species. The resultant Al and Ti species were barely active for olefin polymerization,<sup>337,342,366</sup> and thus, the ligand transfer reaction was identified as a deactivation path, which appeared to be general for this class of complex.<sup>188,354,366,374-377</sup> In fact, devastating effects of  $\text{AlMe}_3$  on polymerization activity

and syndiospecificity were reported, especially when the catalysts were in contact with MAO in the absence of an olefin monomer.<sup>163,164,366,375-377,379</sup>

The cationic methyl species  $[(\text{L}^{\text{FI}})_2\text{TiMe}]^+/\text{[MAO]}^-$  (**57**) can polymerize ethylene and propylene to form a  $(\text{L}^{\text{FI}})_2\text{Ti}(\text{polymethyl})^+$  species **59** in NMR tubes. The polymethyl species **59** are again  $C_2$ -symmetric and thermally more stable toward the said ligand transfer reaction, probably due to the steric protection by the bulky polymethyl group (Scheme 21). A slightly different Ti species that showed similar downfield shift of the imine proton was obtained from **56**/ $\text{AlMe}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ , with concomitant formation of  $\text{Ph}_3\text{CMe}$ , suggesting that a similar cationic species was generated.

Subsequently in 2005, Talsi and co-workers carried out more intensive studies on the same bis(phenoxy-imine) Ti complex **56**, using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR and EPR spectroscopy, and they fully characterized the species described above and other intermediates.<sup>367</sup> They suggested that, at lower Al/Ti ratios below 50,  $(\text{L}^{\text{FI}})_2\text{TiMeCl}$  was formed and that it was in equilibrium with  $(\text{L}^{\text{FI}})_2\text{TiMe}^+$ , which was in keeping with the observation made for  $(\text{L}^{\text{FI}})_2\text{TiMeBr}$  (**52**) and  $[(\text{L}^{\text{FI}})_2\text{TiMe}]^+/\text{[B}(\text{C}_6\text{F}_5)_4]^-(53)$  described above.<sup>153</sup> At the higher Al/Ti ratios in the 50–500 range,  $(\text{L}^{\text{FI}})_2\text{TiMe}^+$  prevailed. The downfield-shifted imine proton of  $(\text{L}^{\text{FI}})_2\text{TiMe}^+$  was decoalesced into two peaks at  $-20^\circ\text{C}$  (coalesced at  $-5^\circ\text{C}$ ), from which it was proposed that  $C_2$  symmetry collapsed by weakly coordinated solvent molecules (S) to the open site of  $(\text{L}^{\text{FI}})_2\text{TiMe}^+$ . The  $\Delta G^\ddagger$  for the solvent association/dissociation process was estimated at 12.5 kcal/mol. The cationic methyl species was decomposed by (1) ligand transfer to  $\text{AlMe}_3$  to form  $(\text{L}^{\text{FI}})\text{AlMe}_2$  (**58**), as discussed above, and (2) reduction of Ti(IV) to a paramagnetic Ti(III) species, which was confirmed by EPR. The growing polymethyl species was also characterized using the  $^{13}\text{C}$ -labeled species and  $^{13}\text{C}_2\text{H}_4$ , and the  $\alpha$ -carbon of the titanium-bound methylene group ( $\text{Ti}-^{13}\text{CH}_2-$ ) was observed at 111.5 ppm. Activation with **56**/ $\text{AlMe}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  was also examined.

Subsequently, they extended the study to other related complexes, including  $(\text{L}^{\text{FI}})(\text{pyrrolyl-imine})\text{TiCl}_2$  (**37**)<sup>375</sup> and  $(\text{L}^{\text{FI}})_2\text{ZrCl}_2$  (**60**, **61**, **62**; Chart 7).<sup>377</sup> For the Zr complexes, it was proposed that the nature of the ion pairs varied from OSIPs to the heterobinuclear cationic complexes of the type  $[(\text{L}^{\text{FI}})_2\text{ZrMe}(\mu\text{-Me})\text{AlMe}_2]^+$ , depending on the size of the  $\text{R}^2$  groups.

Another important form for the activation of bis(phenoxy-imine) group 4 metal complexes can be performed using  $^3\text{Bu}_3\text{Al}$  and  $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ . In the activation of metallocenes, this method allows a metallocene halide to be alkylated and then activated into a cationic alkyl species simultaneously, thereby skipping the synthesis and isolation of metallocene dialkyls.

Chart 7

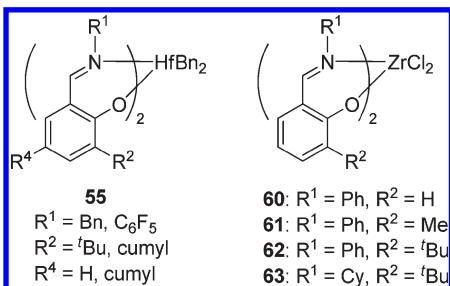
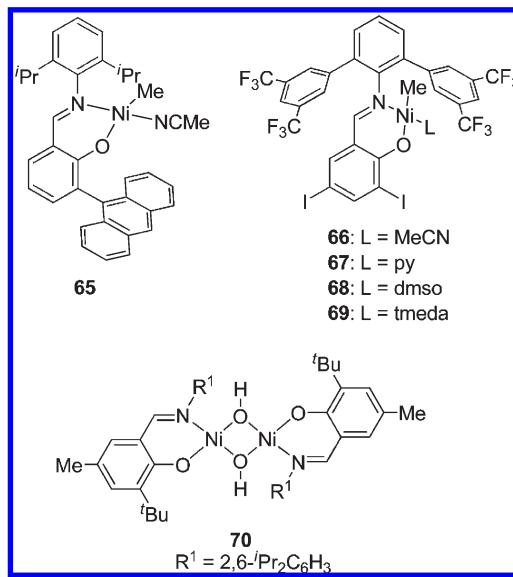


Chart 8



However, when this method was applied to bis(phenoxy-imine) group 4 metal complexes instead of MAO activation, all of the evidence points to the in situ generation of a new species, where the imine is reduced to an amine by  ${^t}\text{Bu}_3\text{Al}$  (in these experiments, bis(phenoxy-imine) group 4 metal complexes and  ${^t}\text{Bu}_3\text{Al}$  are mixed for 10 min before polymerization). The resulting phenoxy-amine complexes exhibited a number of interesting polymerization characteristics owing to their unusual N donors,  ${^t}\text{Bu}_2\text{Al}-\text{N}$ , being bulkier and weaker donors than the imine-nitrogen. In general, phenoxy-amine species are lower in polymerization activity than the corresponding phenoxy-imine species, but they tend to polymerize olefinic monomers into extremely high molecular weight polymers (see sections 4.1.2, 4.1.3, and 6.1).

Liu et al. reported that  $\text{R}_3\text{Al}$  ( $\text{R}$ : methyl, ethyl, *n*-hexyl) alone could activate complexes **62** and **63** at high to very high activities for ethylene polymerization, up to about 60 kg-polymer/(mmol-M·h·bar).<sup>380</sup> When  ${^t}\text{Bu}_3\text{Al}$  or  $\text{Et}_2\text{AlCl}$  was used instead, these complexes were completely inactive. The molecular weight of the obtained polymers was much higher than that obtained with MAO activation but exhibited very large molecular weight distributions ( $M_w/M_n$  3–70), indicating that multiple active centers were generated. The active species showed low capability for 1-hexene incorporation.

**3.2.2. Activation and Active Species of Phenoxy-Imine Ni Complexes.** Mono(phenoxy-imine) Ni(II) complexes,  $(\text{L}^{\text{FI}})\text{-NiX(L)}$ , are usually prepared from Ni(II) precursors such as  $[\text{NiX(Ar)}(\text{PPh}_3)_2]$  ( $\text{X}$ : Cl, Br; Ar: Ph, *o*-tolyl, 1-naphthyl, etc.),  $[\text{NiMe}_2(\text{TMEDA})]$ , and  $[\text{NiCl}(\eta^3\text{-benzyl})(\text{PMMe}_3)]$  (see section 2.2.6). Therefore, Ni–C bonds are already installed, and there is no need for alkylation. What is required to activate these Ni complexes is to dissociate the neutral ligand from the Ni center, for which  $\text{Ni}(\text{cod})_2$  or  $\text{B}(\text{C}_6\text{F}_5)_3$  are often used as a scavenger (cocatalyst). In one example, it was demonstrated that copper(I) halides can be used for that purpose in aqueous media.<sup>268</sup> The dissociation and recombination of L donors are supposed to be in equilibrium throughout polymerization reactions, and therefore, the activation process to be discussed below is relevant to initiation as well as propagation.

DFT calculations on the phosphine dissociation energy by Ziegler revealed that the bulkiness of  $\text{R}^2$  substituents such as 9-anthracyl significantly decreased the dissociation energy, because  $\text{R}^2$  is situated ortho to the phenolic oxygen, which is cis to the phosphine.<sup>381</sup> Accordingly, the size of  $\text{R}^1$  had little effect (trans to the phosphine), although the electron withdrawing  $\text{R}^4$  slightly decreased the energy. The dissociation energy of various neutral donors with oxygen was also calculated to mimic the polymerization with additives, and again the dissociation

energy was correlated with the TOF of the catalysts.<sup>382</sup> A correlation between the net charge on Ni and the dissociation energy was also suggested by calculations.<sup>284</sup>

Marks and co-workers demonstrated that a class of dinuclear complexes **21** and **22** prepared from a naphthalene-1,8-diol-based Schiff base ligand **64** and the corresponding nickel complexes (Scheme 22), which were designed for the two Ni centers to be located in proximity, showed modest activities for ethylene polymerization without any cocatalysts, presumably as a result of enhanced phosphine dissociation due to the steric constraints caused by the bimetallic structures.<sup>132,134</sup>

Using  $[\text{NiMe}_2(\text{tmdea})]$  as a precursor in the presence of a labile donor, phosphine free complexes,  $(\text{L}^{\text{FI}})\text{NiMe(L)}$  ( $\text{L}$ : labile donor such as MeCN, pyridine, dimethyl sulfoxide, tmdea) (**65**–**69**; Chart 8), are accessible, which can act as single component catalysts without the need for phosphine scavenging cocatalysts, and exhibit significantly higher activity than phosphine-coordinated catalysts due to less coordinating ability of MeCN,<sup>87</sup> pyridine,<sup>67,69</sup> DMSO,<sup>298</sup> or TMEDA<sup>299</sup> to the Ni center.

Mecking and co-workers prepared a series of Ni complexes, whose affinity to water was varied by L donors.<sup>70</sup> They found that the complexes bearing hydrophilic or amphiphilic L ligands showed higher activity in water than in toluene. They rationalized that this was because once the L was dissociated in water, the active site enclosed in polymer nanoparticles became so lipophilic that recoordination of the hydrophilic L was significantly disfavored and thus water served as a scavenger in these examples.

Bis-ligated Ni complexes  $(\text{L}^{\text{FI}})_2\text{Ni}$  are inactive toward ethylene polymerization, generally speaking.<sup>87,192,264</sup> Nevertheless, it has been known that  $(\text{L}^{\text{FI}})_2\text{Ni}$  or related Ni(II) complexes can be active for ethylene oligomerization upon activation with cocatalysts such as MAO or alkylaluminums in the presence of olefins, where they are assumed to be transformed into mono(phenoxy-imine)Ni alkyl olefin complexes.<sup>80,264,312,314,315,383–385</sup> This catalyst system appears to be active also for the polymerization of MMA,<sup>305,313</sup> styrene,<sup>307</sup> norbornene (NBE),<sup>317,318,386,387</sup> and the copolymerization of ethylene and MMA,<sup>306</sup> but different mechanisms are possibly involved in some instances.<sup>388,389</sup>

Binuclear  $\mu$ -(OH)<sub>2</sub>-bridged Ni complexes,  $(L^{FI})Ni\{\mu\text{-(OH)}_2\}-Ni(L^{FI})$  (**70**), were found to be activated with nearly equimolar amounts of alkylaluminums or alkyllithiums for ethylene polymerization.<sup>316</sup> The activities were slow but stable and long-lasting. Interestingly, the activities were not significantly different in polar solvents (THF or dioxane) or in toluene. In addition, the polymerizations are apparently first order with respect to [ethylene], implying a somewhat different mechanism from those of the other Ni or Pd catalyzed (neutral or cationic) ethylene polymerizations, which exhibit zeroth order dependence to [ethylene] (vide infra).<sup>16,390,391</sup> It was proposed for this rather unusual behavior that coordination of aluminum or lithium cocatalysts (R—M') to the phenolic oxygen formed a heterobinuclear complex, which serves as a catalyst resting state.

### 3.3. Chain Propagation Reaction

During insertion polymerization via the generally accepted Cossee—Arlman mechanism,<sup>392,393</sup> the rate-determining steps are usually different for early and late metal-based complexes due to the difference in resting states. For cationic Pd complexes, alkyl olefin complexes are often spectroscopically observable as a resting state, which are followed by the rate-determining olefin insertion step. Accordingly, the rate law of the polymerizations is usually zeroth order in monomers.<sup>16,390,391</sup> On the other hand, it is difficult to see an olefin  $\pi$ -complex in the early metal catalyzed polymerization. The resting states will be an electron deficient cationic metal—alkyl species stabilized by  $\beta$ -agostic interaction or the coordination of weak nucleophiles such as counteranions, alkylaluminums, solvents, neutral catalyst precursors, and so on (see ref 394 and references therein). The polymerizations usually demonstrate first or higher order dependence with respect to monomers. However, translation of the apparent monomer dependence is never easy due to the existence of a complex equilibrium of the ion pairs involving the other nucleophiles in the reactions.

In the polymerization catalyzed by phenoxy-imine ligated complexes, the general polymerization characteristics for early or late metals seem to be unchanged. In the  $C_2$ -symmetric octahedral framework of *cis*-N/*trans*-O/*cis*-X group 4 metal complexes, the X—M—X fragment becomes chemically equivalent. Therefore, the Cossee—Arlman mechanism can be applied without complications. However, the tetrahedral  $(L^{FI})NiX(L)$  complexes have an unsymmetrical environment to the X—Ni—L moiety, and thus, there are at least two insertion pathways, depending on the arrangements of O, N, X, and L in the square planar geometry. DFT calculations suggest that, although the complex bearing the alkyl group trans to the O is more stable than trans to the N for the alkyl ethylene complex, the insertion barrier is substantially low (10 kcal/mol,<sup>381</sup> 7.7 kcal/mol<sup>395</sup>) for the complex with the alkyl group trans to the N compared to trans to the O.<sup>381,395,396</sup> Therefore, isomerization of the alkyl olefin complex from *trans*-O to *trans*-N before insertion was expected to precede ethylene insertion (calculated  $\Delta E$  for the isomerization: 11.4 kcal/mol,<sup>381</sup> 8.0 kcal/mol<sup>395</sup>). Such *cis*—*trans* isomerization was indeed observed for **65** and **68** bearing labile L ligands.<sup>87,298</sup> The barrier for the isomerization was estimated to be about 17 kcal/mol, and a unimolecular process via a tetrahedral intermediate was suggested. It was proposed that ethylene insertion may be assisted by  $\alpha$ -agostic interaction, which is not common for late metal based catalysts.<sup>395</sup> The  $\alpha$ -agostic interaction was also suggested for a methyl acrylate (MA) insertion product.<sup>397</sup> Agostic interactions were also studied for propylene insertion to  $(L^{FI})M-\text{Ph}$  (M: Ni, Pd) using DFT calculations.<sup>398</sup>

It was tentatively considered that  $NiR(PPh_3)$  (R: alkyl or H) species would be in a resting state because no free phosphine was observed during polymerization by NMR<sup>264</sup> and the molecular weights and the activities were increased by raising ethylene pressure (0.7–1.7 MPa), accompanied with decrease of chain branching.<sup>81,82,264,265</sup> However, the kinetic order of the catalysts with respect to ethylene becomes zeroth order in ethylene at higher ethylene pressure (>3.0 MPa).<sup>296</sup>

Direct observation of catalytic ethylene dimerization was made for  $(L^{FI})NiMe(\text{dmso})$  (**68**).<sup>298</sup> The observed resting state of the reaction was  $(L^{FI})NiEt(\text{dmso})$ , which exhibited higher activity than the methyl precursor toward ethylene insertion. In the flask scale polymerization, the polymerization activity of **68** was about 1.2 kg-polymer/(mmol-M·h) in the range 1.0–3.0 MPa of ethylene monomer, meaning that the activity was independent of the ethylene concentration.

There are many examples in which electron withdrawing substituents increased the polymerization activity for both early and late metal phenoxy-imine complexes (For early metals, see refs 91, 159, 168, and 222; for late metals, see refs 123, 272, 273, 288, 294, 383, 399, and 400). This electronic effect presumably stems from increased propagation rate due to the enhanced electrophilicity of the metal center, which decreases the insertion barrier.<sup>284,381</sup>

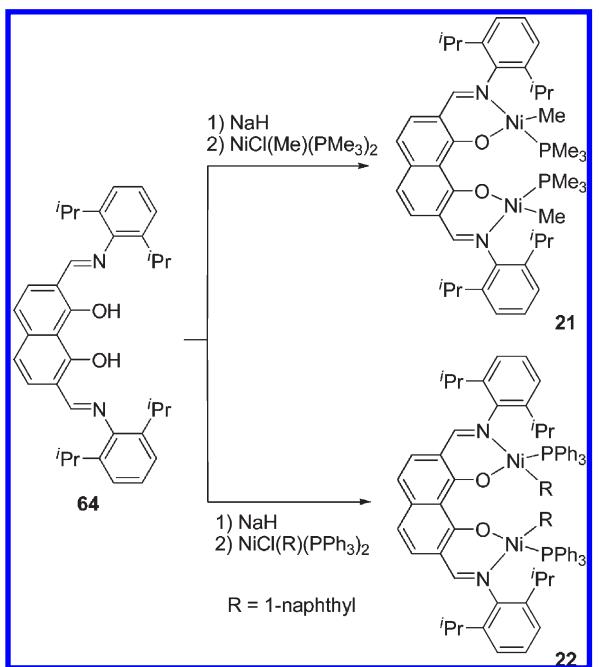
### 3.4. Irreversible Deactivation

The heteroatoms of phenoxy-imine ligands can be vulnerable to Lewis acidic components in the reaction media. The ligand transfer to  $Me_3Al$  in MAO (see section 3.2.1) is probably triggered by interaction of  $Me_3Al$  with the phenolic oxygen, followed by C—H bond activation by the M—C species. As described above, the nucleophilicity of the imine appears to be significantly enhanced by its coordination to metal,<sup>189</sup> and the imine moiety is easily reduced by intramolecular migration of the metal-bound alkyl groups<sup>42,100,112,149,151,152,226,227,236,360</sup> or by the alkylaluminums added as an activator.<sup>43,161,205,215,222,229,230,235,401,402</sup> This vulnerability is especially serious for more electrophilic early metals than late metals.

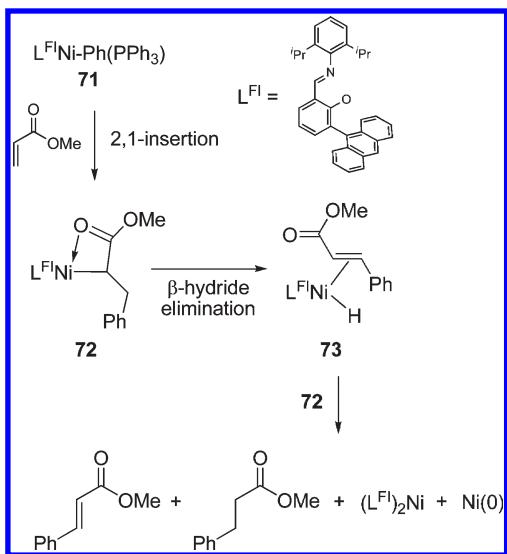
For the Ni complexes, formation of bis-ligated complex  $(L^{FI})_2Ni(\text{II})$ , which is considered to be a thermodynamic sink, causes irreversible deactivation. In the presence of methyl acrylate (MA), the catalyst  $(L^{FI})NiPh(PPh_3)$  (**71**) afforded an olefin, *trans*- $\text{PhCH=CHCOOMe}$ , as well as the saturated  $\text{PhCH}_2\text{CH}_2\text{COOMe}$ , and concurrent formation of  $(L^{FI})_2Ni(\text{II})$  was observed. The proton for the saturated product appeared to come from MA, for which it was proposed that hydride transfer from the olefin nickel hydride  $(L^{FI})\text{Ni-H(olefin)}$  (**73**) to  $(L^{FI})\text{NiCH(COOMe)(CH}_2\text{Ph)}$  (**72**) yielded R—H,  $(L^{FI})_2Ni(\text{II})$ , and  $\text{Ni(0)}$  species either via direct (bimolecular) hydride transfer or via  $(L^{FI})-\text{H}$  generated through reductive elimination of  $(L^{FI})\text{Ni-H(olefin)}$  (Scheme 23).<sup>403,404</sup> This is considered to be a reason why this class of Ni catalysts are not successful in the copolymerization of ethylene with vinyl-functionalized monomers.

More recently, Berkefeld and Mecking carried out an in-depth study on deactivation processes in ethylene polymerization using  $(L^{FI})NiMe(\text{dmso})$  (**68**).<sup>298</sup> They found that **68** was decomposed, presumably into  $\text{Ni(0)}$ , along with liberation of ethane via a bimolecular elimination reaction. For a higher alkyl Ni complex,  $(L^{FI})NiR(L)$ , which is always equilibrated with  $(L^{FI})\text{NiH}(L)$ , the alkyl complex is involved in the decomposition in a bimolecular fashion, but homo-cross-coupling between the alkyl species

Scheme 22

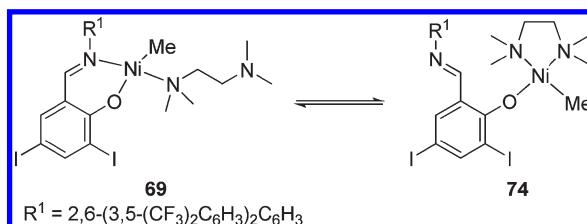


Scheme 23

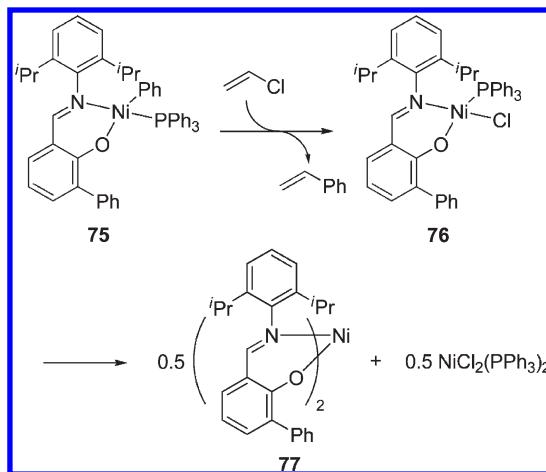


larger than ethyl was not observed, indicating the steric sensitive nature of this bimolecular reaction. Hydrolysis by water was a minor deactivation path relative to this bimolecular deactivation. Similar bimolecular decomposition pathways were confirmed for  $(\text{L}^{\text{FI}})\text{NiMe}(\text{tmeda})$  (69) in an ethylene dimerization reaction.<sup>299</sup> Despite the labile nature as a coordinating L, tmeda can displace the imine donor of the phenoxy-imine ligand to form  $(\kappa^1\text{-}\text{L}^{\text{FI}})\text{NiMe}(\kappa^2\text{-tmeda})$  (74) in equilibrium with  $(\text{L}^{\text{FI}})\text{NiMe}(\kappa^1\text{-tmeda})$  (69) (Scheme 24). The  $\kappa^2$ -tmeda species appears to be inactive to ethylene insertion but actively involved in the bimolecular deactivation process and also susceptible to hydrolysis, in contrast to the water-tolerant  $(\text{L}^{\text{FI}})\text{NiMe}(\text{dmso})$  (68).

Scheme 24



Scheme 25



With regard to the species, which is supposed to be involved in copolymerization with vinyl-functionalized monomers such as MA or vinyl acetate (VA), it was again suggested that the Ni(II) hydride mediated decomposition was operative.<sup>397</sup> MA reacted more rapidly than ethylene with  $(\text{L}^{\text{FI}})\text{NiH}(\text{PMe}_3)$  to generate the species  $(\text{L}^{\text{FI}})\text{NiCH}(\text{COOMe})\text{Me}$  via 2,1-insertion (not observed), which was stable in the absence of the Ni(II) hydride at  $-40^\circ\text{C}$  but did not insert either MA or ethylene and rapidly decomposed to  $\text{MeCH}_2(\text{COOMe})$  above  $0^\circ\text{C}$ . VA was more slowly inserted into the nickel hydride complex via 1,2-insertion to form a kinetic product, which was decomposed to a Ni(II) acetate species via  $\beta$ -acetate elimination from the thermodynamically favored 2,1-inserted product.

Polymerization of vinyl chloride (VC) was attempted by Jordan and co-workers using a typical  $(\text{L}^{\text{FI}})\text{NiPh}(\text{PPh}_3)$  complex 75.<sup>405</sup> In a <sup>1</sup>H NMR experiment, it was observed that  $\text{PPh}_3$  was slowly displaced by VC, and the 1,2-insertion of VC into the Ni–Ph bond followed by  $\beta$ -Cl elimination afforded styrene and  $(\text{L}^{\text{FI}})\text{NiCl}(\text{PPh}_3)$  (76), which was eventually turned into  $(\text{L}^{\text{FI}})_2\text{Ni}$  (77) and  $\text{NiCl}_2(\text{PPh}_3)_2$  by disproportionation (Scheme 25). Even in the presence of ethylene, the  $\beta$ -Cl elimination appeared to prevail and no polymer was obtained.

### 3.5. Ligand Design for Highly Active Phenoxy–Imine Catalysts

From the discussions in each section above, there appears to be common catalyst designs for early and late metal phenoxy–imine complexes for activity toward olefin insertion. The most obvious is sterically demanding substituents at the imine nitrogen ( $\text{R}^1$ ) and ortho to the phenolic oxygen ( $\text{R}^2$ ).

First, these substituents are required for both systems to sustain catalytically active geometries. They are necessary for the group 4 metal bis(phenoxy-imine) complexes to take geometries that bear cis-oriented X ligands, whereas, for the Ni phenoxy-imine complexes, the substituents prevent formation of inactive bis-ligated complexes.

Second, bulky R<sup>2</sup> substituents increase the catalytic activity. Intrinsically, olefin polymerization catalysts have the latent coordination site at the electron deficient metal center, for which olefin monomers must compete against other potential coordinating species in the polymerization media such as L donors, counteranions, neutral catalyst precursors, alkylaluminums,  $\beta$ -agostic hydrogen, and so on. Bulky R<sup>2</sup> substituents can enhance dissociation of such coordinating species and shift the equilibrium to the olefin-coordinating species. Simultaneously, R<sup>2</sup> substituents will protect the vulnerable phenolic oxygens from the Lewis acidic species, coordination of which sometimes causes irreversible deactivations such as ligand transfer to alkylaluminums. Another role of the R<sup>2</sup> substituents was suggested by calculations. They showed that the olefin  $\pi$ -complex was significantly destabilized by large R<sup>2</sup> substituents but the energy level of the subsequent transition state of olefin insertion remained at a similar level to the control (with small R<sup>2</sup>), which lowered the overall insertion barrier for the complex with large R<sup>2</sup> substituents.<sup>406</sup>

Third, bulky R<sup>1</sup> substituents generally increase the molecular weight of the polymer incidentally for both early and late metal complexes, although this apparently similar trend actually stems from different mechanisms. This will be discussed in sections 4.1 and 4.2 in more detail, but it is considered to be a general trend for early and late metals and not specific to phenoxy-imine ligated complexes. For group 4 metal bis(phenoxy-imine) complexes, bulky R<sup>1</sup> substituents give significant spatial constraints to the X–M–X moiety, which destabilizes a six-membered ring transition state for  $\beta$ -H transfer to the coordinating olefin relative to a more compact four-membered transition state for propagation. On the other hand, bulky R<sup>1</sup> substituents on nickel mono(phenoxy-imine) complexes are thought to block the axial faces of the square planar Ni center, thereby retarding the associative chain transfer from the Ni olefin  $\pi$ -complexes.

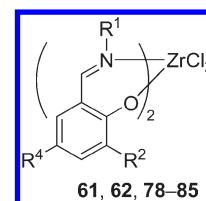
Fourth, electron withdrawing substituents generally increase the polymerization activity of phenoxy-imine complexes, which is not necessarily true for metallocene catalysts. The difference between phenoxy-imine ligated complexes and metallocenes might come from the fundamental difference in bonding properties between metal and ligands, that is, heteroatom based M–(O, N) bonds and carbon based M–Cp' bonds.

## 4. POLYMERIZATION WITH PHENOXY-IMINE COMPLEXES

### 4.1. Group 4 Metal Complexes

**4.1.1. Ethylene Polymerization.** The catalytic performance of prepared complexes for olefin polymerization is most often measured by ethylene polymerization because the simplicity of ethylene monomers allows for estimation of the basic performance of the catalyst, such as activity and molecular weight capability, and also for assessing the impact of systematic variants, such as metal center, ligand substituents, activators, polymerization conditions, and so on. Historically, the breakthrough discovery of a highly active ethylene polymerization catalyst, whose activity was usually several orders higher than its predecessor,

**Table 4. Effects of the Substituents of the Phenoxy-Imine Zr Complexes on Ethylene Polymerization Activity<sup>a</sup>**



complex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	activity [kg-polymer/(mmol·M·h)]
<b>61</b>	Ph	Me	H	0.4
<b>78</b>	Ph	<i>i</i> Pr	H	0.9
<b>62</b>	Ph	<i>t</i> Bu	H	519
<b>79</b>	Ph	<i>t</i> Bu	Me	331
<b>80</b>	Ph	1-adamantyl	Me	714
<b>81</b>	Ph	cumyl	Me	2096
<b>82</b>	Cy	<i>t</i> Bu	Me	82
<b>83</b>	Cy	1-adamantyl	Me	434
<b>84</b>	Cy	cumyl	Me	4315
<b>85</b>	Cy	CPh <sub>2</sub> Me	H	6552

<sup>a</sup> Polymerization conditions: toluene, 250 mL; MAO, 1.25 mmol; Al/Zr = 250–625,000; ethylene 0.1 MPa; 25 °C; 5 or 10 min.

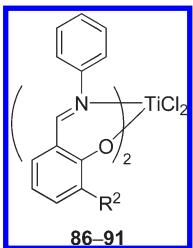
almost always brought product and/or process innovations to the industry, and, thus ethylene polymerization has been the primary method for catalyst evaluation at many laboratories. It should be noted, however, that the activities obtained at each institution are often not directly comparable due to the many possible instrumental and technical fluctuations (for example, ref 17). Therefore, the activity numbers in this article should be treated as not too strictly comparable to each other, particularly for cross-referential comparisons.

**4.1.1.1. Functions of R<sup>2</sup> Substituents.** The relative ease of synthesis and the modular property of phenoxy-imine ligands allow for systematic study into the effects of each substituent for diversified steric and electronic ligand structures. As discussed in section 3, the substituents ortho to the phenolic oxygen (R<sup>2</sup>), which are placed above and below the reaction site (the X–M–X moiety), have a pronounced impact on both polymerization activity and the molecular weight of the obtained polymers.

Fujita and co-workers have revealed a keen relationship between the size of the R<sup>2</sup> and the ethylene polymerization activity for a series of (L<sup>FI</sup>)<sub>2</sub>ZrCl<sub>2</sub> complexes **61**, **78**, **62**, and **79–85** (Table 4).<sup>24,204,205,214</sup> Remarkable leaps in activity were found between *i*Pr and *t*Bu and also between *t*Bu and cumyl. For R<sup>1</sup> = cyclohexyl, the second leap becomes more pronounced relative to R<sup>1</sup> = phenyl, and the activity reaches 6552 kg-polymer/(mmol·M·h·bar) when R<sup>2</sup> = CPh<sub>2</sub>Me (complex **85**). This activity corresponds to a TOF of 64,900 s<sup>-1</sup> bar<sup>-1</sup>, standing as one of the most efficient catalysts in any catalytic reaction. The complexes having methyl para to the phenolic oxygen (R<sup>4</sup> substituents) consistently show slightly lower activity than the unsubstituted complexes (R<sup>4</sup> = H) (complex **79** vs **62**), although the reason is not clear.

With regard to the titanium (L<sup>FI</sup>)<sub>2</sub>TiCl<sub>2</sub> complexes, the similar but modest increase in polymerization activity along with the larger R<sup>2</sup> (**86** < **87** < **88**) can be seen with the exceptions that R<sup>2</sup> = phenyl (complex **90**) and silyl groups (complexes **89** and **91**)

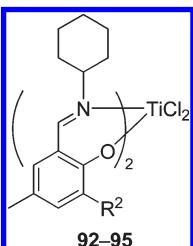
**Table 5. Effects of the R<sup>2</sup> Substituents of the Phenoxy–Imine Ti Complexes on Ethylene Polymerization Activity and the Molecular Weight of the Obtained PE<sup>a</sup>**



complex	R <sup>2</sup>	activity [kg-polymer/(mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
86	H	0.038	66	3.13
87	Me	0.246	402	1.54
88	<sup>t</sup> Bu	3.240	1281	2.55
89	TMS	2.666	1105	2.51
90	Ph	4.6	60.4 <sup>c</sup>	
91	SiPh <sub>2</sub> Me	2.5	37.5 <sup>c</sup>	

<sup>a</sup> Polymerization conditions: toluene, 250 mL; MAO, 1.25 mmol; Al/Ti = 250–1250; ethylene, 0.1 MPa; 25 °C; 30 min. <sup>b</sup> Determined by GPC (polystyrene calibration). <sup>c</sup> M<sub>v</sub>.

**Table 6. Effects of the R<sup>2</sup> Substituents of the Phenoxy–Imine Ti Complexes on Ethylene Polymerization Activity<sup>a</sup>**

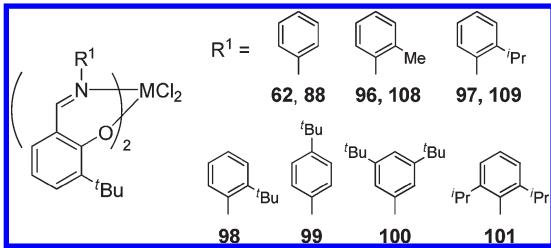


complex	R <sup>2</sup>	T <sub>p</sub> <sup>b</sup> (°C)	activity [kg-polymer/(mmol·M·h·bar)]	M <sub>v</sub> (kg/mol)
92	<sup>t</sup> Bu	30	2.225	1090
		50	1.27	800
93	cumyl	30	6.4	780
		50	3.07	660
		70	2.18	670
94	2-isobornyl	30	0.15	940
		50	0.115	600
95	trityl	30	0.0295	
		50	0.0522	

<sup>a</sup> Polymerization conditions: toluene, 50 mL; ethylene, 0.3 MPa; complex 1.1–2.2 μmol; MAO/Ti = 250–500; 40–60 min. <sup>b</sup> Polymerization temperature.

(Table 5).<sup>156,163</sup> A significant increase of polymer molecular weights accompanied the activity increase. A similar trend was observed for (L<sup>FI</sup>)<sub>2</sub>TiCl<sub>2</sub> complexes 92–95, possessing the cyclohexyl group at R<sup>1</sup> by Ivanchev and co-workers (Table 6).<sup>195,196</sup> In living polymerization with N-fluoroaryl Ti complexes, which will be discussed in detail in the section below, the complex

**Table 7. Effects of the R<sup>1</sup> Substituents of the Phenoxy–Imine Zr and Ti Complexes on Ethylene Polymerization Activity and the Molecular Weight of the Obtained PEs<sup>a</sup>**



complex	M	activity [kg-polymer/(mmol·M·h)]	M <sub>v</sub> × 10 <sup>-4</sup> (g/mol)
62	Zr	519	0.9
96	Zr	40	32
97	Zr	58	113
98	Zr	0.1	>274
99	Zr	271	0.7
100	Zr	244	2.6
101	Zr	~0	
88	Ti	3.24	50.2 <sup>b</sup>
108	Ti	0.301	16.6 <sup>b</sup>
109	Ti	0.186	22.9 <sup>b</sup>

<sup>a</sup> Polymerization conditions: toluene, 250 mL; MAO, 1.25 mmol; complex, 0.02–0.5 μmol; ethylene, 0.1 MPa; 25 °C; 5–30 min. <sup>b</sup> M<sub>n</sub> × 10<sup>-4</sup>, determined by GPC (polystyrene calibration).

bearing R<sup>2</sup> = <sup>t</sup>Bu demonstrated far higher activities in ethylene polymerization (5–10 times) than the complexes with R<sup>2</sup> = cyclohexyl, <sup>i</sup>Pr, Me, and H.<sup>407</sup> Considering that all the polymerizations were strictly living and the initiation efficiencies were nearly quantitative, these results suggested that the steric bulk at R<sup>2</sup> substituents actually increased the propagation rate constant.

These R<sup>2</sup> effects are corroborating the geometry and the reaction mechanisms discussed in section 3; that is, a bulky R<sup>2</sup> should maintain coordinative unsaturation of the metal center, protect the phenolic O-donor from side reactions, and destabilize the olefin π-complex, thereby lowering the olefin insertion energy.

**4.1.1.2. Functions of R<sup>1</sup> Substituents.** In a framework of the *cis*-N/*trans*-O/*cis*-X geometry, substituents on the imine nitrogen (R<sup>1</sup>) are situated at the skewed back side of the reaction site and, thus, embrace the reaction site from the back side of the metal. R<sup>1</sup> substituents are known to exhibit significant influence on the molecular weight of the obtained polymers.

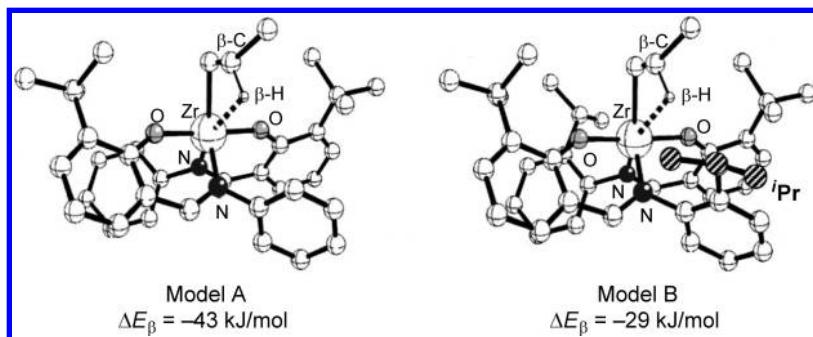
A series of N-aryl groups were examined by Fujita and co-workers for zirconium phenoxy–imine complexes 62 and 96–101 (Table 7).<sup>24,204,205,408,409</sup> By increasing the size of the ortho-substituents of the N-aryl groups, the molecular weights of PE increase in the order H < Me < <sup>i</sup>Pr < <sup>t</sup>Bu at the expense of activity, which decreases progressively in the opposite order, and complex 101 (R<sup>1</sup> = 2,6-diisopropylphenyl) is barely active, presumably because R<sup>1</sup> becomes too large. No such dramatic changes were observed for *meta*- or *para*-<sup>t</sup>Bu substitution.

The relationship of R<sup>1</sup> and the molecular weight is also assured when alkyl groups are used as R<sup>1</sup>, which allows us to go toward the lower molecular weight region by employing smaller alkyls than a phenyl group (Table 8).<sup>24,214,220,408,409</sup> The relationship

**Table 8.** Effects of the Substituents of the Phenoxy–Imine Zr Complexes on Ethylene Polymerization Behavior<sup>a</sup>

complex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	activity [kg-polymer/(mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	vinyl end <sup>c</sup> (%)
63	Cy	<sup>t</sup> Bu	H	87.7	14	1.7	90
102	2-methylcyclohexyl	<sup>t</sup> Bu	H	93.0	290	4.9	71 <sup>d</sup>
103	Cy	1-adamantyl	Ph	142.4	24	1.8	84
104	2-methylcyclohexyl	1-adamantyl	Ph	52.5	960	4.1	33 <sup>d</sup>
105	cyclopentyl	<sup>t</sup> Bu	H	67.2	3.6	2.1	96
106	cyclobutyl	<sup>t</sup> Bu	H	31.6	2.0	1.7	95
107	cyclopropyl	<sup>t</sup> Bu	H	50.4	4.4	2.0	91

<sup>a</sup> Polymerization conditions: toluene, 250 mL; ethylene, 0.1 MPa; 25 °C; 5 min; DMAO, 0.625 mmol; complex, 0.5 μmol. <sup>b</sup> Determined by GPC (polyethylene calibration). <sup>c</sup> Degree of vinyl unsaturation at one of the two polymer chain ends, determined by <sup>1</sup>H NMR. <sup>d</sup> Determined by IR.



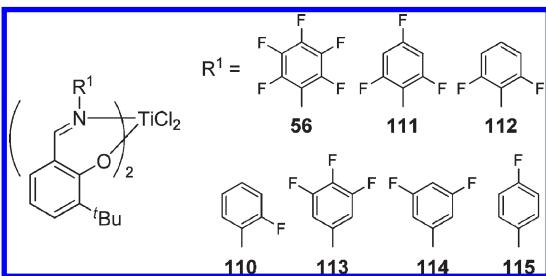
**Figure 5.** Stabilization energies ( $\Delta E_{\beta}$ ) as a result of  $\beta$ -agostic interaction. Cationic complex models A and B stand for the active species generated from complexes **62** and **97**, respectively. All hydrogens except the  $\beta$ -hydrogen are omitted for clarity. An *n*-propyl group is employed as the model of a polymer chain. Reproduced with permission from ref 205. Copyright 2001 American Chemical Society.

between **63** and **102** can be reasonably compared to that between **62** and **96**; that is, the methyl group at the 2-position of cyclohexyl or phenyl groups significantly increased polymer molecular weights by 1 order of magnitude. This holds true for other combinations of R<sup>2</sup> and R<sup>4</sup> (**103**, **104**). Interestingly, depression of the activity by the methyl group was little or modest for aliphatic R<sup>1</sup> groups. With a smaller R<sup>1</sup> than cyclohexyl, i.e., cyclopentyl, cyclobutyl, or cyclopropyl (complexes **105**–**107**), the molecular weights of polyethylenes decrease significantly to reach the order of 10<sup>3</sup>, and the PEs have very high vinyl chain-end contents. As a matter of fact, the PEs of this molecular weight range with high vinyl-end group contents have been unavailable by other means,<sup>410,411</sup> and these vinyl-terminated PEs have found unique material applications<sup>412,413</sup> (see section 10.3.2).

DFT calculations on **62** and **97** suggest that the  $\beta$ -agostic structure for the latter was destabilized by the *ortho*-isopropyl groups by 14 kJ/mol (Figure 5), which rendered **97** less prone to a  $\beta$ -H transfer reaction than **62**.<sup>205</sup> In fact, **62** afforded vinyl-terminated PEs in high yields, whereas **97** generated PEs with saturated chain ends, because chain transfer to alkylaluminums becomes the main chain transfer reaction instead of the infeasible  $\beta$ -H transfer path.<sup>414</sup>

Moreover, DFT calculations on **63** and **105**–**107** have revealed that these complexes favor the  $\beta$ -H transfer reaction via a bimolecular path, i.e.,  $\beta$ -H transfer to the coordinating monomer, over a unimolecular transfer to the Zr center by  $\Delta\Delta E = 48$ –58 kJ/mol mainly due to the extremely unstable nature of the (L<sup>Pt</sup>)<sub>2</sub>Zr–H species. In line with these calculations, it was found that, for the Zr complexes, the molecular weights of PEs were independent of ethylene pressures, while the activity showed the first order dependence on the monomer concentration.<sup>220</sup> In addition, DFT calculations suggest that Zr complexes favored a front-side ethylene insertion (an ethylene molecule approaches to a  $\beta$ -agostic resting state from the side of the  $\beta$ -H-metal bond). The front-side approach for propagation will go part of the way with the  $\beta$ -H transfer to the coordinating monomer, making both processes competitive with each other.<sup>415</sup> That is, whether or not the  $\beta$ -agostic hydrogen is displaced by a coordinating ethylene, the  $\beta$ -agostic resting state will form either the four-centered transition state for the propagation or the six-centered transition state for the chain transfer. Since the R<sup>1</sup> substituents are situated at the skewed back side of the reaction sites within a framework of *cis*-N/*trans*-O/*cis*-X geometry commonly found for these complexes (see section 3.1.1), it is likely that the larger R<sup>1</sup> substituents destabilize the six-centered

**Table 9. Effects of the R<sup>1</sup> Substituents of the Phenoxy–Imine Ti Complexes on Ethylene Polymerization Behavior<sup>a</sup>**



complex	activity [kg-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
56	18.12	424	1.13
111	2.43	145	1.25
112	0.828	64	1.05
110	0.127	13	1.06
113	44.6	98	1.99
114	32.0	129	1.78
115	5.31	128	2.18

<sup>a</sup> Polymerization conditions: toluene, 250 mL; MAO, 1.25 mmol; complex, 0.4–5.0 μmol; ethylene, 0.1 MPa; 100 L/h; 1–5 min; 50 °C. <sup>b</sup> Determined by GPC (polyethylene calibration).

transition state more than the four-centered transition state and that the higher rate of the propagation relative to the chain transfer results in higher molecular weight polymers. In fact, the X-ray structures of the bis(phenoxy–imine) Zr complexes have demonstrated that the Cl–Zr–Cl bond angles were narrowed as R<sup>1</sup> substituents became larger: R<sup>1</sup> = cyclobutyl (**106**: 100.64(3) $^{\circ}$ ), cyclohexyl (**63**: 99.8(2) $^{\circ}$ ), 2-methyl-cyclohexyl (**102**: 98.00(6) $^{\circ}$ ).<sup>220</sup>

The R<sup>1</sup> effect discussed above demonstrates that one can control the chain-end structures (and molecular weights) of the polymers by suitably selected R<sup>1</sup> substituents, producing either exclusively vinyl- or Al-terminated PEs.<sup>46,413</sup> These polymers are extremely versatile precursors for the chain-end-functionalized polymers, which will be discussed in section 10.3.2.

Let us move to the (L<sup>F1</sup>)<sub>2</sub>TiX<sub>2</sub> complexes, which have the inherent nature to afford much higher molecular weight PEs than the corresponding Zr congeners discussed above. The high molecular weight capability may be attributable to the smaller ionic radius of Ti<sup>4+</sup> (0.68 Å) than that of Zr<sup>4+</sup> (0.86 Å), which makes the Ti metal more shielded and packed by the surrounding phenoxy–imine ligands. Generally speaking, the more crowded the metal gets, the higher-molecular-weight polymers the complex tends to form.<sup>416</sup> There is a study in which the differences between Ti and Zr were argued based on the crystal field theory.<sup>417</sup>

Despite these intrinsic differences between Ti and Zr, it is quite interesting to note that the R<sup>1</sup> substituents of the Ti complexes again possess the ability to control chain transfer processes but in a rather unexpected manner.

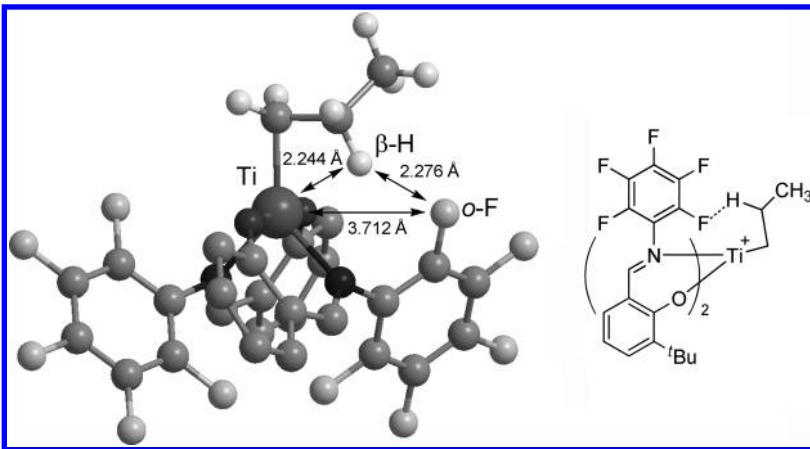
Comparison between **88** (R<sup>1</sup> = phenyl), **108** (R<sup>1</sup> = *o*-tolyl), and **109** (R<sup>1</sup> = *o*-isopropylphenyl) exhibited no apparent molecular weight increase that was seen for the Zr congeners, although the activity depression by the ortho-alkyl groups was similar to that of the Zr complexes (Table 7).<sup>163</sup> Assuming equally efficient initiation (the concentration of the active species is close to

the concentration of the precursors), stable activity, and time-independent molecular weights, the ratios of activities and molecular weights can be roughly correlated with the frequency of the sum of chain terminations, albeit under limited circumstances. Now, the ratios (apparent chain termination frequency: F<sub>CT</sub>) for the three complexes, *o*-H (6450) ≫ *o*-Me (1810) > *o*-<sup>i</sup>Pr (810), appeared to indicate that the ortho-alkyls retard the rates of both propagation and chain terminations, but more significantly for the latter. A similar trend was also observed for 2,6-dialkyl substituted N-aryl groups.<sup>146,195,196</sup> In fact, the molecular weight distribution for **109** exhibits a relatively small value (PDI 1.29), suggesting that it may take on a living polymerization character, presumably due to the extremely slow rate of any chain terminations. Therefore, the functions of the ortho-alkyls, which are mostly steric in nature, appear to be similar to those for the Zr complexes, i.e., the ortho-alkyls discourage chain transfer reactions more than they do propagation reaction, thereby affording higher molecular weight polymers.

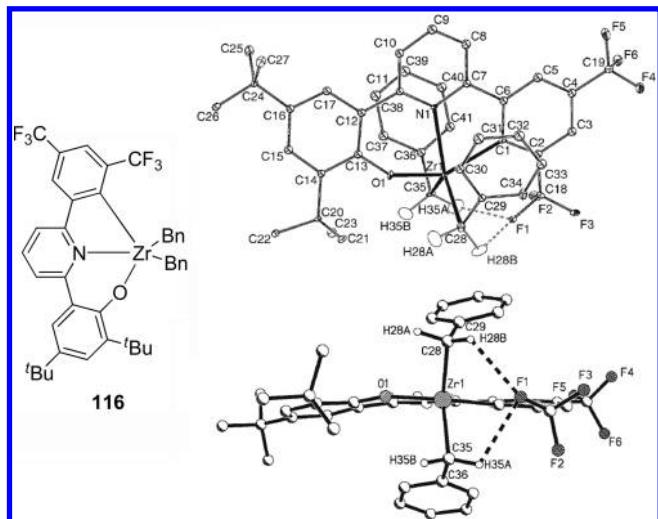
Introduction of an *ortho*-fluorine to N-aryl groups (complex **110**) also decreases the activity,<sup>24,45,160</sup> even more significantly than the ortho-alkyls, despite the smaller size of the fluorine atom, implying that a simple steric argument will not suffice. The polymerization data for the Ti complexes **56**, **110**, and **111–115**, bearing fluoroaryl R<sup>1</sup> groups, are compiled in Table 9. It is evident that the activity depression is observed only for the *ortho*-F substituted complexes when compared with the meta- or para-fluorinated complexes having the same numbers of fluorine(s). The complexes having *meta*- and/or *para*-fluorine(s) (complexes **113–115**) exhibited higher activity than **88**, and the activities increase as the number of fluorines increases. This holds true for a series of *ortho*-fluorinated complexes, and the activity of complex **56** bearing a perfluorophenyl group as R<sup>1</sup> far exceeds that of **88** (activity: 4.15 kg-polymer/(mmol·M·h·bar) under similar polymerization conditions<sup>160</sup>). The most distinctive and prominent feature is that the *ortho*-fluorinated complexes exhibit typical living polymerization characteristics at ambient temperature or higher despite the large excess of MAO that is a potential chain transfer agent.<sup>24,45,158,160,372,373</sup> The molecular weights proportionally increase with polymerization time; all the while, the PDI values are kept narrow. On the other hand, the meta- or para-fluorinated complexes demonstrate ordinary nonliving polymerizations (PDI ~2).

Living olefin polymerization catalysts have been available in the past.<sup>10,48,63,418–445</sup> However, when considering the limitations they imposed for their livingness (low polymerization temperatures to suppress side reactions and thereby low TOF, limitation of applicable monomers and achievable molecular weight of polymers, etc.), the living nature of these Ti complexes at temperatures much higher than room temperature for both ethylene and propylene (see section 4.1.2 for living propylene polymerization) is truly remarkable. In particular, the living polymerization with **56** is extraordinary in that it exhibits very high TOF, comparable to that of nonliving Cp<sub>2</sub>ZrCl<sub>2</sub>, and the living propagating species is stable for at least 1 h at ambient temperature in the absence of monomers.<sup>160</sup> It should be underlined that efficient and practical syntheses of various unique olefinic block polymers are not possible without this robust living nature (see sections 4.1.3 and 10.4).

As mentioned earlier, the titanium bis(phenoxy–imine) complexes inherently afford high molecular weight polymers and the ortho-alkyl substitution further intensifies the nature by sterically impeding the chain transfer reactions at the expense of activity.



**Figure 6.** DFT-optimized structure of a cationic *n*-propyl species derived from **56** (see inset figure). Phenolic aryl groups are simplified for clarity. Reproduced with permission from ref 27. Copyright 2009 American Chemical Society.

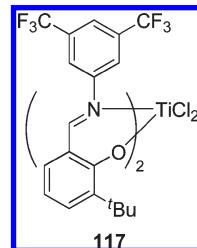


**Figure 7.** Top: Perspective view of **116** from the neutron diffraction study (50% probability ellipsoids) showing selected hydrogen atoms. Bottom: View along the Zr1–N1 vector. Reproduced with permission from ref 448. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

In fact, as suggested above for **109** or in other examples, the bis(phenoxy-imine) Ti complexes sometimes indicated signs of a living polymerization, albeit unsatisfactorily, under the limited conditions (at or below ambient temperature, in a short polymerization time, for example).<sup>89,160,163,446</sup> However, when considering the differences of fluorine and alkyls in size and in the degree of livingness, the role of the *ortho*-F atom could not be justified by simple steric effects.

A rationale for the robust livingness brought by the *ortho*-F was proposed by Fujita and co-workers based on DFT calculations on the cationic species bearing an *n*-propyl group as a propagating alkyl group.<sup>24,45,160,372,373</sup> The calculations revealed a  $\beta$ -agostic resting state, in which one of the *ortho*-F(s) was situated at close proximity to the  $\beta$ -hydrogen on the *n*-propyl chain ( $\sim 2.3 \text{ \AA}$ ) (the van der Waals radii of H and F are 1.20 and 1.47  $\text{\AA}$ , respectively) (Figure 6). What is more interesting is that an attractive and electrostatic interaction can be expected between the negatively charged *ortho*-F and the positively charged  $\beta$ -H. As evidence,

### Chart 9

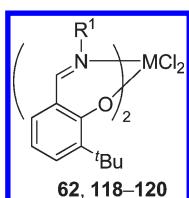


elongation of the  $\text{H}_\beta-\text{C}$  bond was also observed and the electrostatic energies of the  $\text{C}-\text{F}\cdots\text{H}_\beta-\text{C}$  interaction were estimated to be around 30 kJ/mol for these *ortho*-fluorinated Ti complexes. This means that the  $\beta$ -agostic state, a potential intermediate for  $\beta$ -hydrogen chain transfer reactions, is electronically stabilized by the *ortho*-F, which can be attributed to the unusually high stability at high temperature. The extra stabilization imposed by the *ortho*-F on the  $\beta$ -agostic resting state can virtually eliminate the chain transfers from the polymerization, but it seems to slow down the propagation as well (**88** vs **110**). However, the additional F(s) at meta- or para-positions to the *ortho*-fluorinated complexes appeared to selectively accelerate the propagation without impairing the *ortho*-F stabilization toward the chain transfer reactions. If the back-side monomer approach (from the opposite side of the  $\beta$ -agostic  $\text{H}-\text{M}$  bonding) is assumed, the monomer would be able to coordinate the Ti center without significantly disrupting the  $\beta$ -agostic structure that is stabilized by the *ortho*-F and then move to the transition state for monomer insertion in a concerted manner.<sup>45</sup> All together, **56** bearing a perfluorophenyl  $\text{R}^1$  group becomes a highly active and extremely robust living polymerization catalyst.

The *ortho*-F derived living polymerization of bis(phenoxy-imine) Ti complexes appeared to be general irrespective of the other substituents, such as  $\text{R}^2$  or  $\text{R}^4$ .<sup>166,373</sup>

With regard to the hypothetical  $\text{C}-\text{F}\cdots\text{H}-\text{C}$  interaction, Chan and co-workers experimentally proved by using NMR spectroscopy and X-ray and neutron crystallography that the  $\text{C}-\text{F}\cdots\text{H}-\text{C}$  interaction was indeed feasible in the solid state and in solution for some phenoxy-pyridine Zr complexes (for example, **116**) bearing a cyclometalated aryl group (Figure 7).<sup>447,448</sup>

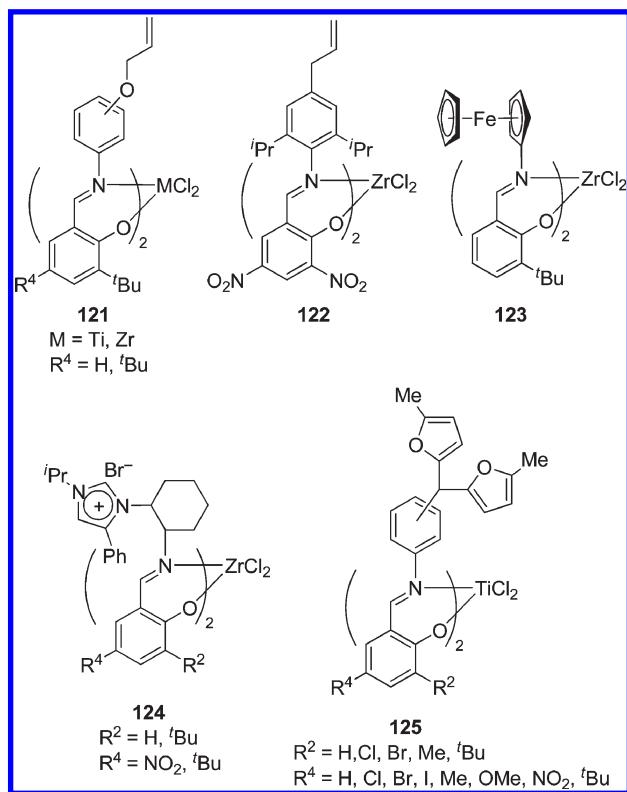
**Table 10. Effects of the R<sup>1</sup> Substituents of the Phenoxy–Imine Zr and Hf Complexes on Ethylene Polymerization Behavior<sup>a</sup>**



complex	R <sup>1</sup>	M	activity [kg-polymer/(mmol-M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
118	C <sub>6</sub> F <sub>5</sub>	Zr	335	157.2	1.90
119	C <sub>6</sub> F <sub>5</sub>	Hf	28.8	409.6	2.70
62	Ph	Zr	224	7.3	
120	Ph	Hf	21.4	16.8	

<sup>a</sup> Conditions: toluene, 250 mL; complex, 0.1–0.5 μmol; DMAO, 1.25 mmol; ethylene, 100 L/h; 5 min; 25 °C. <sup>b</sup> Determined by GPC (polyethylene calibration).

**Chart 10**



Furthermore, Mecking and co-workers revealed that a structurally closely related Ti enolatoimine complex bearing an *ortho*-F(s) N-aryl group was an excellent ethylene living polymerization catalyst, whereas the corresponding complexes having *ortho*-methyl-substituted or nonsubstituted N-aryl groups were not performing as living catalysts.<sup>150,203</sup>

As mentioned earlier, the R<sup>1</sup> substituents can electronically enhance the polymerization activity by introducing electron-withdrawing groups. In particular, complexes 114, 113, and 117

(Chart 9) bearing fluorine or CF<sub>3</sub> groups at the meta-position of the N-aryl groups exhibit a >10-fold activity increase relative to 88.<sup>24,45,159</sup> This is presumably due to the increased electrophilicity of the metal, which would lower the insertion barrier. The influences of perfluorophenyl groups were examined also for the Zr and Hf complexes (118, 119, 62, 120) (Table 10).<sup>217</sup> The perfluorinated Zr or Hf complexes do not perform living polymerizations like their Ti congener. However, a significant increase in activity and in the molecular weight of the PE is observed when compared with the case of the non-fluorinated Zr and Hf complexes, which is similar to the Ti complex. Since Zr and Hf are larger than Ti, the distances of *ortho*-F and β-H (~2.48 Å) are longer than that of the Ti complex (~2.3 Å) but still in a range of the attractive interaction assumed for the Ti (the sum of the van der Waals radius of H and F is 2.67 Å). In fact, the F<sub>CT</sub> values, as a measure of apparent chain termination frequency, diminish significantly for the fluorinated Zr and Hf complexes (118: 2130, 119: 70, 62: 30,680, 120: 1270).

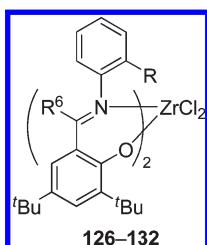
Attempts to incorporate functional groups to the R<sup>1</sup> substituent were made in the hope that such groups can interact with activators or can be used as self-immobilized catalysts 121–125 (Chart 10, for self-immobilization, see section 9.4).<sup>170,201,207,208,211,449</sup>

In summary, R<sup>1</sup> substituents exercise their molecular weight controlling ability from the back side of the reaction site through nonbonding repulsive or attractive interactions, thereby affording polymers in a wide range of molecular weights with desired chain-end structures and enabling extremely robust and versatile living polymerizations. In addition, electron-withdrawing groups can electronically enhance the polymerization activity by making the metal center more electrophilic.

**4.1.1.3. Functions of R<sup>6</sup> Substituents.** The bis(phenoxy–ketimine) Ti and Zr complexes that appeared in the first patent filed by Mitsui Chemicals exhibited low to moderate activity (60–200 g-polymer/(mmol-M·h·bar) at 25 °C) but afforded high molecular weight PEs ([η]: 8–23 dL/g), independently of the metal centers.<sup>19</sup> However, they have been less extensively investigated than bis(phenoxy–imine) complexes, mainly because the activities are not as high and the syntheses are not as straightforward as those for the phenoxy–imine complexes.

Coates and co-workers prepared a series of bis(phenoxy–ketimine) Ti complexes (R<sup>6</sup> = Me, Et, Ph, CF<sub>3</sub>) and examined the ethylene polymerizations.<sup>89</sup> They confirmed that the R<sup>6</sup> substituents greatly reduced the polymerization activities relative to the control (R<sup>6</sup> = H). Moreover, it was also revealed that these complexes, including the control having no substituents at the imine carbon, demonstrated living polymerization characteristics under the conditions examined despite lack of the *ortho*-fluorine, by which they questioned the said *ortho*-F stabilizing effects. However, these results are not necessarily contradictory of the *ortho*-F effects when considering the intrinsic high molecular weight capability of the Ti complexes as mentioned above (see section 4.1.1.2). On the contrary, on closer inspection of the available data with the understanding that care must be taken for a direct comparison, one can still assume that there might be substantial differences in the quality of livingness between the *ortho*-F and the non-F complexes. The *ortho*-fluorinated complexes<sup>150,160</sup> can afford living PEs with much higher molecular weights (mostly over 100 kg/mol, and one example up to 990 kg/mol) at much higher activities (up to >40 kg-polymer/(mmol-M·h·bar)) or in longer polymerization time at high polymerization temperatures (15 min at 50 °C for most cases, 15 min at 75 °C for a Ti enolatoimine complex), while the

**Table 11. Effects of the R<sup>6</sup> and R Substituents of the Phenoxy–Imine Zr Complexes on Ethylene Polymerization Behavior<sup>a</sup>**



complex	R <sup>6</sup>	R	activity [kg-polymer/(mmol-M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
126	H	H	1.6	12	1.43
127	Me	H	12.9	89	1.97
128	Et	H	41.2	40	2.07
129	Ph	H	20.1	31	1.72
130	2-FC <sub>6</sub> H <sub>4</sub>	H	216.3	165	2.43
131	Ph	Me	1.7	104	3.84
132	Ph	F	33.9	71	2.76

<sup>a</sup> Polymerization conditions: toluene, 100 mL; complex, 0.02–0.2 μmol; MAO, Al/Zr = 6000; ethylene, 0.1 MPa; 10 min; 20 °C.

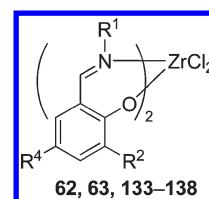
<sup>b</sup> Determined by GPC (polystyrene calibration).

non-fluorinated complexes examined here exhibited lower activities (mostly below 1 kg-polymer/(mmol-M·h) for phenoxy–ketimine complexes), which were evaluated in shorter polymerization time or at lower temperatures (10 min at 0 °C, 1 or 3 min above 20 °C, 8 min at 50 °C for one example) under reduced ethylene concentrations (10 psi = 69 kPa), and therefore, they only gave lower molecular weight polymers (below 100 kg/mol). In fact, Fujita and co-workers previously demonstrated that even a non-fluorinated prototypical Ti complex **88** showed quasi-living polymerization characteristics (PDI = 1.12) under similar conditions (25 °C, 1 min).<sup>163</sup> Thus, they were evaluated in considerably different regions in terms of polymerization conditions and polymer molecular weights. If equivalent conditions were applied, it is not unreasonable to assume that the *ortho*-F complexes would show an admittedly higher aptitude for living polymerization. Either way, a simple dichotomization such as *ortho*-F/living and non-F/nonliving is a false concept and is not what the proposed *ortho*-F effects represent.

A series of Zr complexes **126–132** that have R<sup>6</sup> substituents were also examined for ethylene polymerization upon activation with MAO (Table 11).<sup>92</sup> Although the activity of the control (R<sup>6</sup> = H) appeared to be somehow lower than that expected from complex **62**,<sup>212</sup> the R<sup>6</sup> substituents were generally beneficial for increasing the activities, and the molecular weights of the obtained PEs were always higher than that of the control. Particularly, when the 2-fluorophenyl group was employed as R<sup>6</sup> (complex **130**), the activity and the molecular weight reached the highest value, 216 kg-polymer/(mmol-M·h·bar) and 165 kg/mol (M<sub>w</sub>, polystyrene calibration). The *ortho*-substituents of the N-aryl groups (complexes **131** and **132**) increased the molecular weights in a similar manner to that for the phenoxy–imine complexes.

**4.1.1.4. Functions of R<sup>4</sup> Substituents.** Fujita and co-workers investigated the R<sup>4</sup> substituents (para to the phenolic oxygen) of

**Table 12. Effects of the Substituents of the Phenoxy–Imine Zr Complexes on Ethylene Polymerization Behavior<sup>a</sup>**



complex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	T <sub>p</sub> <sup>b</sup> (°C)	activity [kg-polymer/(mmol-M·h)]	M <sub>v</sub> × 10 <sup>-4</sup> (g/mol)
<b>62</b>	Ph	<sup>t</sup> Bu	H	50	1192	4.7
				75	209	10.0
<b>138</b>	<i>n</i> -hexyl	<sup>t</sup> Bu	H	50	346	1.1
				75	140	2.0
<b>63</b>	Cy	<sup>t</sup> Bu	H	50	751	1.5
				75	211	3.0
<b>133</b>	Ph	<sup>t</sup> Bu	OMe	50	328	36.3
				75	220	22.7
<b>134</b>	<i>n</i> -hexyl	<sup>t</sup> Bu	OMe	50	454	9.9
				75	1008	3.8
<b>135</b>	Cy	<sup>t</sup> Bu	OMe	50	818	16.8
				75	1462	5.4
<b>136</b>	<i>n</i> -hexyl	cumyl	OMe	75	7078	3.9
<b>137</b>	Cy	cumyl	OMe	75	7224	10.4

<sup>a</sup> Polymerization conditions: *n*-heptane, 500 mL; complex, 0.05–0.2 μmol; ethylene, 0.9 MPa; MAO, 1.25 mmol; 15 min. <sup>b</sup> Polymerization temperature.

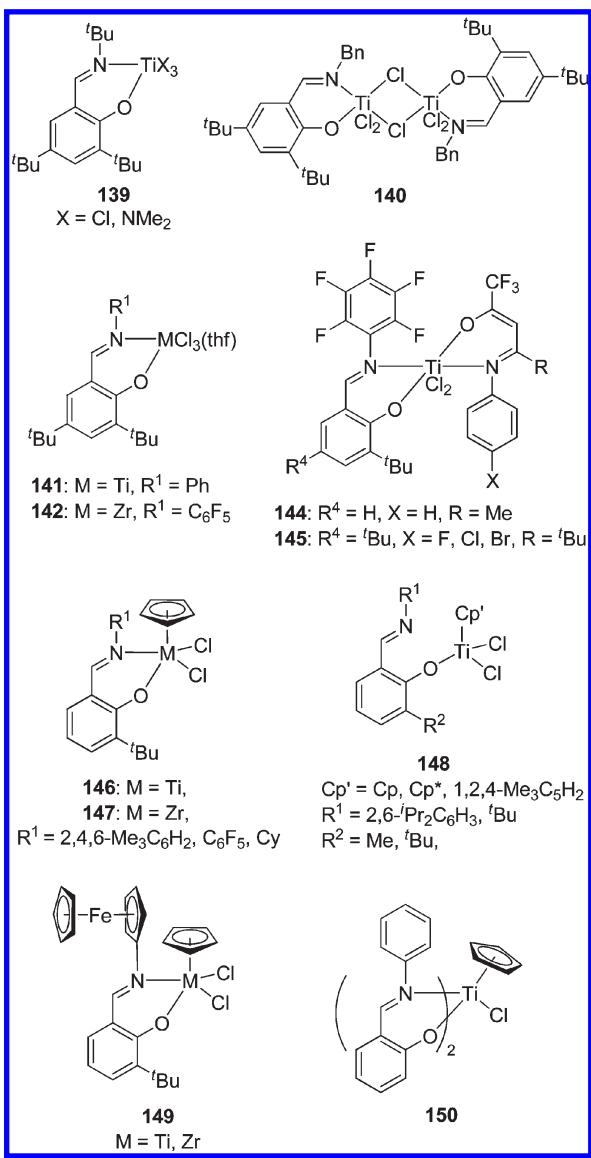
the bis(phenoxy–imine) Zr complexes in the hope that they could improve the thermal stability of the catalysts, whose activities usually start degrading above ~40 °C.<sup>24,213</sup> Indeed, complexes **133–137**, bearing the electron donating methoxy group as R<sup>4</sup>, exhibited improved thermal stability relative to R<sup>4</sup> = H (complexes **62, 63, 138**) (Table 12). Particularly in combination with aliphatic R<sup>1</sup>, the activities at 75 °C became higher than those at 50 °C, reaching 7224 kg-polymer/(mmol-M·h·bar) for **137**, which was one of the highest ever achieved under industrially practical conditions. The reason for this enhanced activity in higher temperature regions is considered to be enhanced stability of the active species, which stems from the strengthened metal–ligand bond owing to the methoxy group. The bond strengthening was confirmed spectroscopically, crystallographically, and computationally. Similar observations were made by Scott and co-workers.<sup>354</sup>

Sun and co-workers prepared a series of Ti complexes, where R<sup>4</sup> was varied. Since a bulky 2,6-diisopropylphenyl group was employed as R<sup>1</sup> (R<sup>2</sup> = H), the complexes exhibited a *trans*-N/*cis*-O/*cis*-X geometry. Nevertheless, electron-withdrawing R<sup>4</sup> substituents significantly increased polymerization activities.<sup>171</sup>

**4.1.1.5. Combination Consisting of Phenoxy–Imine and Other Ancillary Ligands.** Mono(phenoxy–imine) ligated complexes (L<sup>Fl</sup>)MX<sub>3</sub> were prepared for their use in olefin polymerization catalysis and also as a precursor in order to synthesize heteroligated hybrid complexes (see section 2.2.8).

Ladipo and co-workers prepared mono(phenoxy–imine) ligated Ti complexes **139** and **140** in a monomeric (R<sup>1</sup> = <sup>t</sup>Bu) or a dimeric (R<sup>1</sup> = CH<sub>2</sub>Ph) fashion (Chart 11). However, the complexes **139** demonstrated low activities for ethylene polymerization irrespective of X = Cl or NMe<sub>2</sub> (14 or 30 g-polymer/(mmol-M·h·bar)).<sup>101</sup>

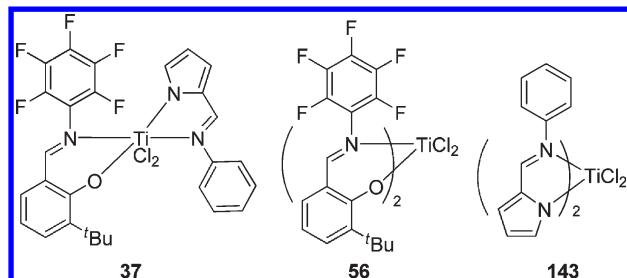
## Chart 11



Likewise, the Ti and Zr monoligated complexes **141** and **142** prepared by Lancaster, Bochmann, and their co-workers exhibited activities up to 440 and 1100 g-polymer/(mmol·M<sup>-1</sup>·h<sup>-1</sup>·bar) in ethylene polymerization.<sup>154,155</sup> From the multimodal molecular weight distributions often observed for the obtained PEs, the authors speculated that disproportionation to bis-ligated complexes might occur during the polymerizations.

Although these results for the monoligated complexes were rather disappointing, the monoligated complexes were soon applied to the synthesis of heteroligated complexes of the type  $(L^{FI})(L)MX_2$ , where L stands for a bidentate monoanionic ligand other than a phenoxy-imine ligand. The first successful example of a heteroligated complex of this kind is a hybrid complex between bis(phenoxy-imine) and bis(pyrrolyl-imine) complexes. Bis(pyrrolyl-imine) complexes, which were developed by Fujita and co-workers, have been known to be a family of highly active catalysts with high comonomer incorporating ability.<sup>50-55</sup> Interestingly, hybrid complex 37 exhibited

Table 13. Ethylene Polymerization Results for the Phenoxy-Imine and Pyrrolyl-Imine Ti Complexes<sup>a</sup>



complex	activity [kg-polymer/ (mmol·M·h)]	$M_w^b$ (kg/mol)	$M_w/M_n^b$
37	89.5	300	2.4
56	35.9	400	4.1
143	6.0	75	2.2

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 5  $\mu\text{mol}$ ; ethylene, 0.1 MPa; MAO, 1.25 mmol; 5 min; 25 °C. <sup>b</sup> Determined by GPC.

significantly higher activity than the original homologated complexes **56** and **143** (Table 13) and also demonstrated higher comonomer uptake (see section 4.1.3).<sup>308,345</sup>

Subsequently, Lancaster and co-workers prepared a series of mixed-ligand complexes having a phenoxy-imine and a  $\beta$ -ketoimine ligand.<sup>347</sup> Complex **144** bearing electron withdrawing  $C_6F_5$  and  $CF_3$  groups at each ligand exhibited high activity toward ethylene polymerization at 5.7 kg-polymer/(mmol-M $\cdot$ h), affording high molecular weight polymers ( $\sim$ 400 kg/mol) with narrow molecular weight distribution. Later, similar complexes **145** were prepared by Li and co-workers and examined for ethylene homo- and copolymerization with NBE.<sup>348</sup> These heteroligated complexes exhibited ethylene polymerization activities comparable to or higher in some examples than those of the parent homoligated complexes in ethylene polymerization (6–10 kg-polymer/(mmol-M $\cdot$ h)). These complexes also demonstrated living polymerization characteristics in ethylene/norbornene copolymerization (see section 4.1.3.2).

Fujita and co-workers reported that a titanium complex **40** bearing a phenoxy-ketimine and a phenoxy-ketone was accidentally crystallized from a crude mixture and that the complex was later synthesized in a reproducible manner, namely slow hydrolysis of the parent complex **39** (Scheme 17). The complex exhibited tolerance toward disproportionation in solution and presumably during ethylene polymerization, which was reasonably assumed from the observed single-site polymerization characteristics. However, the activity of the heteroligated complex was lower than that of **39** and the living nature of the parent complex was also lost.<sup>349</sup>

There are several examples of hybrid complexes consisting of phenoxy-imine and cyclopentadienyl groups. Lancaster, Bochmann, and their co-workers synthesized a series of ( $Cp$ )-phenoxy-imine group 4 metal hybrid complexes (( $Cp$ )-( $L^{FI}$ ) $MCl_2$ ; M: Ti, Zr) and examined olefin polymerization using these complexes, **146** and **147**.<sup>190</sup> The phenoxy-imine ligand coordinated to the metal in a bidentate fashion. Upon activation with MAO, these complexes showed low activities (10–100 g-polymer/(mmol·M $\cdot$ h $\cdot$ bar)) to ethylene polymerization. Similar titanium hybrid complexes having a substituted cyclopentadienyl

and a phenoxy-imine ligand of the type  $(Cp')(L^{FI})TiCl_2$  (**148**) were prepared by Nomura, Huang, and co-workers.<sup>352</sup> In their neutral forms, the imine nitrogens did not coordinate to the Ti in all cases, and it was also not ascertained if those nitrogens could participate in the polymerizations in their activated (presumably) cationic forms. These complexes were capable of performing ethylene homopolymerization (0.1–11 kg-polymer/(mmol·M·h)) at 0.4 MPa), syndiospecific styrene polymerization, and copolymerization of ethylene and 1-hexene or norbornene. A similar bridged complex was also reported but exhibited low to moderate activity and broad molecular weight distributions.<sup>110</sup> Complex **149**, which has a ferrocenyl group as  $R^1$ , displayed lower activity than the bis-complex and also showed a multisited character.<sup>208</sup>

The following examples include two phenoxy-imine ligands and a cyclopentadienyl group. Erker and his co-workers prepared a cationic complex,  $[(Cp)_2(L^{FI})Zr]^+[BPh_4]^-$ , although not tested for olefin polymerization.<sup>144</sup> Qian and co-workers synthesized a hybrid complex  $(Cp)(L^{FI})_2TiCl$  (**150**), which exhibited higher ethylene polymerization activity than the corresponding bis(phenoxy-imine) complex **86**, albeit at a low rate of 44 g-polymer/(mmol·M·h).<sup>104</sup>

**4.1.2.  $\alpha$ -Olefin Polymerization.** In  $\alpha$ -olefin polymerization, including propylene as the most important monomer, there are added layers of complexity on the ethylene polymerization, the most representative of which are the regio- and stereochemistry of monomer insertion.

Scientists at Mitsui applied for the comprehensive patent on syndiospecific living propylene and living ethylene polymerizations, and block copolymer synthesis by *N*-fluoroaryl bis(phenoxy-imine) Ti complexes, representing the first examples of syndiospecific propylene polymerization and living ethylene and propylene polymerizations. The patent was filed on January 26, 2000, and internationally laid open on August 2, 2001. Since 2001, they reported on living ethylene and propylene polymerizations based on the Mitsui patent.<sup>450</sup>

Inspired by the results of ethylene polymerization with bis(phenoxy-imine) group 4 metal complexes disclosed by Mitsui in 1999,<sup>156,212</sup> Coates and co-workers started working on Ti-FI catalysts in reference to propylene polymerization and consequently demonstrated that a non-fluorinated version of a bis(phenoxy-imine) Ti complex exhibited syndiospecificity in nonliving propylene polymerizations via a combinatorial approach in 2000 (received on June 13, 2000) and subsequently reported on the living syndiospecific propylene polymerizations with a bis(phenoxy-imine) Ti complex bearing  $C_6F_5$  groups on the imine-nitrogens in 2001 (received on February 23, 2001). Coates and co-workers applied for the patent on syndiospecific (living) propylene polymerization with specific bis(phenoxy-imine) Ti complexes (filed on September 18, 2001).<sup>451</sup> Following the Mitsui's and Coates's discoveries, Pellecchia, Cavallo, Mazzeo, Lamberti, Talarico, and others have been busy researching propylene polymerization with *N*-fluoroaryl bis(phenoxy-imine) Ti complexes.

Stereospecific polymerizations of propylene by stereorigid *ansa*-metallocenes are reasonably well understood as a relationship of the symmetry of metallocene and the stereoselectivity of the resulting PP. More precisely, the orientation of the  $C_\alpha-C_\beta$  bond of the growing M-alkyl species is directed by the chirality at the metal defined by the ancillary ligands, which in turn determines the coordinating face of prochiral propylene so that the propylene methyl group becomes anti to the  $C_\alpha-C_\beta$

bond.<sup>9,364,374</sup> In this scheme (enantiomeric site control),  $C_2$ -symmetric metallocenes, where the  $X_A-M-X_B$  moiety (reaction sites) is homotopic, favor the same prochiral face of the coordinating propylene irrespective of the two sites ( $X_A$  or  $X_B$ ), generating preferentially isotactic sequences. For  $C_s$ -symmetric metallocenes, when assuming regular alternating chain migratory insertions, the enantiotopic reaction sites make an alternating selection of the prochiral face of the propylene, which results in syndiotactic polymers.<sup>9,358</sup>

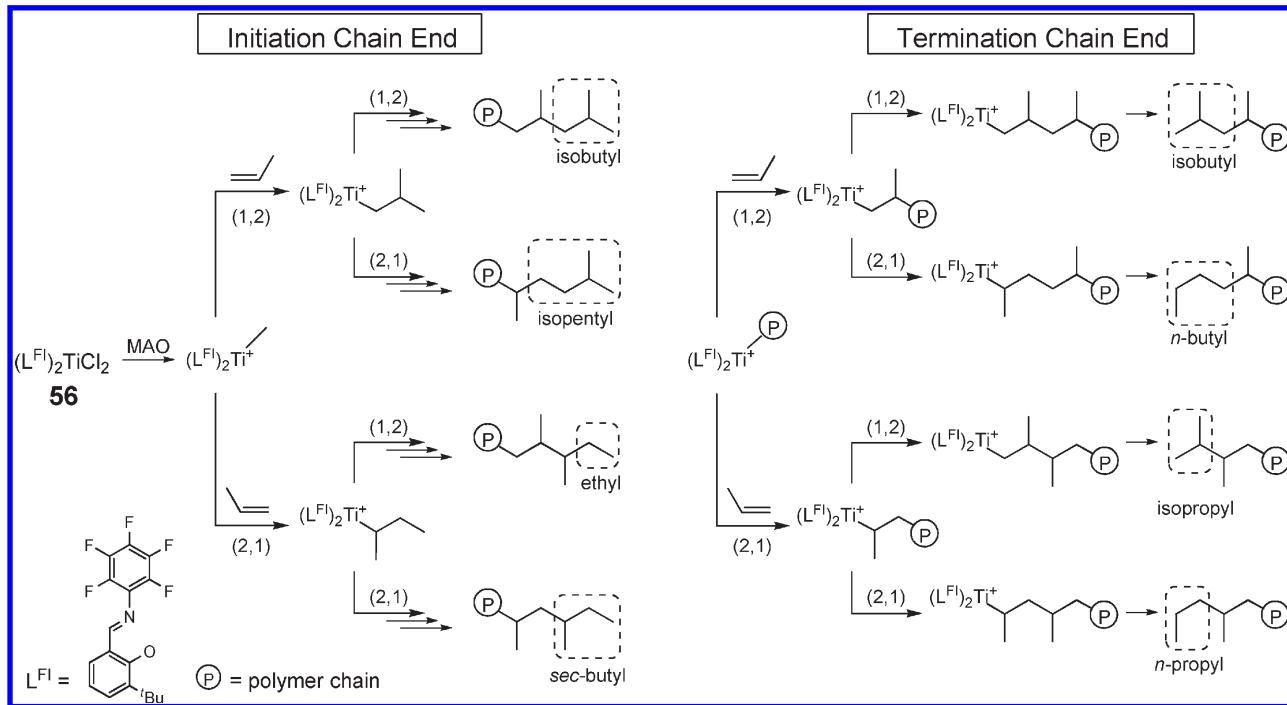
As mentioned earlier in section 3.1.1, most of the bis(phenoxy-imine) group 4 metal complexes have the  $C_2$ -symmetric *cis*-N/*trans*-O/*cis*-X geometry. However, quite unexpectedly, the obtained PPs are found to be atactic to slightly syndiotactic for Zr and Hf complexes and moderately to highly syndiotactic for Ti complexes, when activated with MAO. Furthermore, the stereospecificity was dramatically altered when these complexes were activated with  $'Bu_3Al$  and  $Ph_3CB(C_6F_5)_4$ , i.e., moderately to highly isotactic for Zr and Hf complexes and atactic for Ti complexes.

In this section, these unusual propylene and  $\alpha$ -olefin polymerizations are discussed, focusing on substituent effects and stereo-/regioregulating mechanisms for the syndio- and isospecific polymerizations catalyzed by bis(phenoxy-imine) group 4 metal complexes.

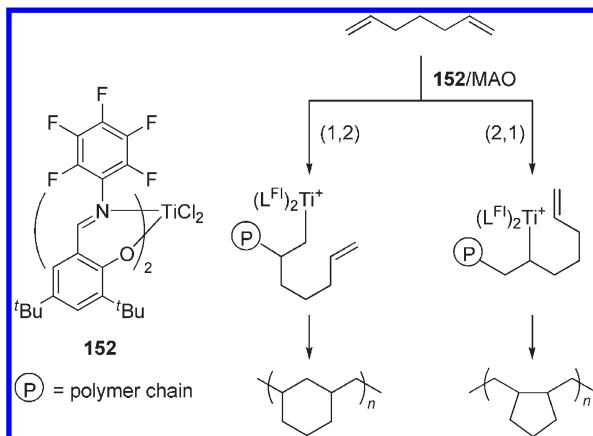
**4.1.2.1. Syndiotactic Polypropylene.** As mentioned above, bis(phenoxy-imine) Ti catalysts afford sPP when activated with MAO. Introduction of the  $C_6F_5$  group as an  $R^1$  substituent significantly enhanced both activity and syndiospecificity,<sup>24,45,85,162,163,408</sup> whereas complex **125** ( $R^1 = 4$ -[bis-(5-methyl-2-furyl)methyl]phenyl,  $R^2 = R^4 = 'Bu$ ) afforded nearly completely atactic PPs (aPP).<sup>452</sup> Cavallo and Poater offered a rationale for the *ortho*-F effects on stereospecificity based on the calculations of the buried volume of the complexes.<sup>453</sup> The  $C_6F_5$  groups filled the key quadrants more effectively than the  $C_6H_5$  groups, indicating that the *ortho*-F sterically enhanced the stereospecificity. Moreover, complexes such as **56** and **152** exhibited excellent living polymerization characteristics at ambient temperatures.<sup>24,45,79,84,85,372,373,418,425,454,455</sup> It should be noted that these complexes also served as remarkable living ethylene polymerization catalysts,<sup>158,160</sup> as discussed in section 4.1.1. The robust livingness toward both ethylene and propylene at ambient temperature or above and the high stereospecificity make these catalysts truly unique because these characteristics create many opportunities for the synthesis of olefinic block copolymers (see section 4.1.3.4). The obtained sPPs were revealed to possess the *rrrm* and *rrmr* pentad sequences as the main source of stereoerrors, indicating that the polymerization apparently followed a chain-end-control mechanism. It was soon found out that the unusual regiochemistry was involved in this propylene polymerization.

First, Fujita and co-workers examined the chain-end structures of a low molecular weight sPP obtained by a living polymerization with **56** for a short polymerization time.<sup>24,85,372,374,408,427</sup> The polymer revealed *n*-propyl, isobutyl, and isopentyl groups in nearly equal intensity, which indicates that the first propylene insertion to  $[(L^{FI})_2TiMe]^+$  species takes place in a 1,2-fashion (Scheme 26). Furthermore, since the *n*-propyl and isopentyl chain ends are relevant to terminating and initiating chain ends, respectively, the composition of these chain-end structures indicates that 2,1-insertion prevailed with about 70% probability in the second monomer insertion as well as in the last two monomer units, implying that the 2,1-insertion is the primary mode of propylene enchainment in this polymerization. This

Scheme 26



Scheme 27

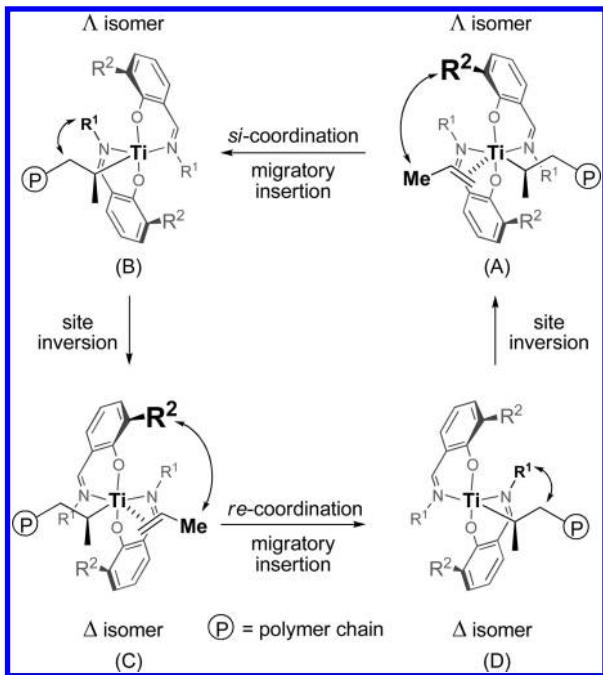


represents the first example of highly regular 2,1-insertion chemistry for early transition metals aside from vanadium catalyzed propylene polymerizations.<sup>456</sup>

Pellecchia and co-workers reached similar conclusions from the chain-end structures for nonliving catalysts **88**, where they identified  $\beta$ -H transfer from the methyl group of the last-2,1-inserted propylene unit, generating allyl-chain ends.<sup>457–459</sup> Since the chain-end structures for the living polymers were below the detection limits, they carried out the copolymerization of propylene with a small amount of <sup>13</sup>C-labeled ethylene (<2 mol %, all the ethylene units were singularly isolated by consecutive propylene units) using living catalysts **56**. The obtained polymers had two consecutive methylene units, far more than the three consecutive methylene units. This means that predominant 2,1-insertions were interrupted by an ethylene unit, which was

followed by a few 1,2-insertions. They also found that the 1,2-insertion after the ethylene unit was nonstereoselective.

Coates and co-workers provided further evidence for this unusual regiochemistry by the analysis of chain-end structures of nonliving polymers as well as the cyclopolymerization of 1,6-heptadiene and ethylene/propylene copolymerizations using a living catalyst **152**.<sup>460,461</sup> The chain-end structures of SPP obtained by **153** again proved to have allyl-chain ends via  $\beta$ -H transfer from the methyl group of the last-2,1-inserted propylene unit, and the ethylene/propylene copolymerizations produced high fractions of even numbered methylene sequences due to the regiorregular 1,2-insertions after the consecutive ethylene sequences, following predominant 2,1-insertions. In the cyclopolymerization of 1,6-heptadiene, the cyclization was found to be quantitative and afforded both methylene-1,3-cyclohexane and



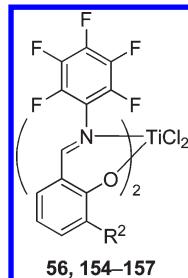
**Figure 8.** Proposed site-inversion mechanism for syndioselective propylene polymerization promoted by phenoxy-imine Ti catalysts. Reproduced with permission from ref 45. Copyright 2005 Elsevier.

ethylene-1,2-cyclopentane units in equal quantity (Scheme 27). Assuming that only 1,2-insertion is sterically allowed for the cyclization process (insertion of the second olefin of the diene), the regiochemistry toward the primary Ti-alkyl species is nearly random.

To summarize these studies, the regiochemistry of bis(phenoxy-imine) Ti complexes varies depending on Ti-bound alkyl groups, that is, (1) exclusive 1,2-insertion to Ti-H (assumed after the  $\beta$ -H transfer) and Ti-Me species; (2) preferential 1,2-insertion to Ti-CH<sub>2</sub>CH<sub>2</sub>-R; (3) regiorandom insertion to Ti-CH<sub>2</sub>CH-RR'; and (4) highly regulated 2,1-insertion to Ti-CH(R')CH<sub>2</sub>-R. This selectivity is consistent with the observed regioblock structures obtained by this class of catalysts.<sup>85,94,373,462</sup>

The calculations suggested for octahedral post-metallocene systems that the balance between steric and electronic effects determined regiochemistry, while for tetrahedral metallocene and constrained geometry Cp-amido complexes (CGCs), the steric effects were decisive.<sup>463–466</sup> In particular, an antibonding interaction between the lone pair of the *trans*-N and the M-C bond that is forming by propylene insertion causes the energy differences of regioselectivity between more electron-donating phenoxy-amine ( $sp^3$  N) and less-electron-donating phenoxy-imine ( $sp^2$  N) ligands. The dependence of the size of metal-bound alkyls (M-R) described above was examined also for R = Me,  $i$ Bu, and  $i$ Pr groups. The energy differences about 2–3 kcal/mol were always observed between M- $i$ Bu and M- $i$ Pr species, and bis(phenoxy-imine) complexes exhibited inversion of regioselectivity for the M- $i$ Pr species, which is consistent with the experimental observations. The metal effects (Ti, Zr, Hf) on the regioselectivity were ascribed to the acidity rather than the size for the examined octahedral complexes, which is opposite for the tetrahedral metallocenes and CGCs.

**Table 14.** Effects of the R<sup>2</sup> Substituents of the Phenoxy-Imine Ti Complexes on Propylene Polymerization Behavior<sup>a</sup>



complex	R <sup>2</sup>	activity [g-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	T <sub>m</sub> <sup>c</sup> (°C)	r <sup>d</sup> (%)
154	H	30.7	189.0	1.51	n.d. <sup>d</sup>	43
155	Me	68.8	260.2	1.22	n.d. <sup>d</sup>	50
156	$i$ Pr	31.1	153.7	1.16	n.d. <sup>d</sup>	75
56	$t$ Bu	3.7	28.5	1.11	137	87
157	TMS	5.9	47.0	1.08	152	93

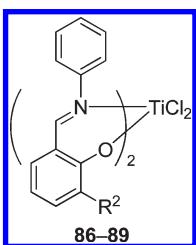
<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 10  $\mu$ mol; MAO, 2.5 mmol; propylene, 0.1 MPa; 25 °C; 5 h. <sup>b</sup> Determined by GPC (polypropylene calibration). <sup>c</sup> Determined by DSC. <sup>d</sup> Not detected.

It is also to be noted that the bis(phenoxy-imine) Ti complex-catalyzed nonliving propylene polymerizations yielded allyl chain ends via  $\beta$ -H transfer from a 2,1-inserted propylene unit almost exclusively, instead of another possible structure, the *cis*-2-but enyl group commonly seen for group 4 metallocene chemistry.<sup>457,460</sup> This nature was successfully applied to the synthesis of allyl-terminated macromonomers.<sup>148,467</sup> The theoretical rationale was given by Caporaso et al.<sup>468</sup>

In light of 2,1-insertion as the principal propagation mode, Cavallo and co-workers proposed based on the combined QM/MM calculations that the observed chain-end-controlled syndiospecificity could be explained by postulating fluxional interconversion between  $\Delta$  and  $\Lambda$  isomers of the octahedral bis(phenoxy-imine) Ti complexes,<sup>364,458,469</sup> which was previously suggested for vanadium-based syndiospecific propylene polymerizations.<sup>470</sup> In the polymerization with  $C_2$ -symmetric bis(phenoxy-imine) Ti complexes, there are four chiral elements, i.e., the asymmetric carbon at the polymer chain end ( $\alpha$ -carbon: *si*-chain and *re*-chain) and the chirality at the metal ( $\Delta$  and  $\Lambda$  isomers), for which four combinations of these chiral elements need to be considered. As shown in Figure 8, the calculations indicated that *re*-chain/ $\Lambda$  isomer A is more stable than *re*-chain/ $\Delta$  isomer D and that *re*-chain/ $\Lambda$  isomer favors propylene coordination at the *si*-face, affording *si*-chain/ $\Lambda$  isomer B (the enantiomer of *re*-chain/ $\Delta$  isomer D) by chain migratory insertion, which isomerizes into more stable *si*-chain/ $\Delta$  isomer C (the enantiomer of *re*-chain/ $\Lambda$  isomer A), which favors propylene coordination at the *re*-face, generating *re*-chain/ $\Delta$  isomer D, which again isomerizes into the more stable *re*-chain/ $\Lambda$  isomer A, coming back right where the whole series of events started. The repetitive cycle of isomerization/insertion certainly affords the syndiotactic sequences of polypropylene.

Significantly, the model also predicted that the monomer *re*/*si*-face selection was made by steric repulsion between the methyl group of the propylene and the R<sup>2</sup> substituent, which was actually observed by Fujita and co-workers.<sup>84,85</sup> In the series of R<sup>2</sup> = H, Me,  $i$ Pr,  $t$ Bu, and Me<sub>3</sub>Si complexes 56, 154–156, and 157,

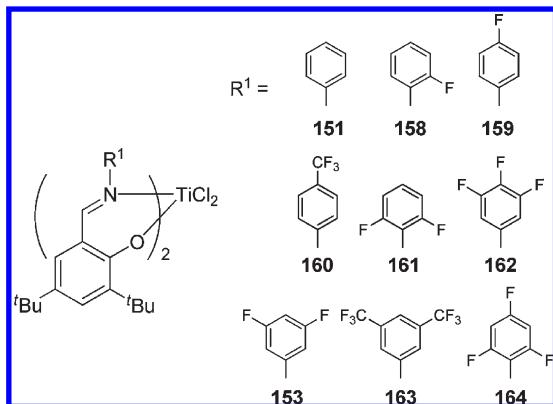
**Table 15. Effects of the R<sup>2</sup> Substituents of the Phenoxy–Imine Ti Complexes on Propylene Polymerization Behavior<sup>a</sup>**



complex	R <sup>2</sup>	activity [g-polymer/(mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	T <sub>m</sub> <sup>c</sup> (°C)	rrrr (%)
86	H	0.40	735/15	2.93/1.51	n.d.	
87	Me	6.70	101	1.47	n.d.	
88	tBu	0.95	6	1.38	97	62.9
89	TMS	1.60	14	1.73	140	83.7

<sup>a</sup> Polymerization conditions: toluene, 350 mL; complex, 0.1 mmol; propylene, 0.37 MPa; MAO, 15 mmol; 6 h; 1 °C. <sup>b</sup> Determined by GPC (polystyrene calibration). <sup>c</sup> Determined by DSC.

**Table 16. Effects of the R<sup>1</sup> Substituents of the Phenoxy–Imine Ti Complexes on Propylene Polymerization Behavior<sup>a</sup>**



complex	yield (g)	activity [g-polymer/(mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	rrrr (%)
151	4.20	1.8	9910	2.14	78
158	0.38	0.16	3220	1.07	52
159	7.20	3.0	18,600	1.75	78
160	6.40	2.7	19,280	2.19	81
161	0.56	0.23	16,410	1.06	83
162	14.30	6.0	9150	2.03	83
153	23.40	9.8	13,580	1.91	81
163	12.10	5.0	14,090	2.17	51
164	2.48	1.0	43,420	1.08	95
152	16.20	6.8	216,610	1.26	96

<sup>a</sup> Polymerization conditions: toluene, 150 mL; catalyst, 0.1 mmol; MAO, 15 mmol; propylene, 40 psi (0.28 MPa); 0 °C; 24 h. <sup>b</sup> Determined by GPC (polystyrene calibration).

a steady increase of the syndiospecificity from 43 to 93% (rr triad, 25 °C) was observed, and the increase was proportional to the calculated volume of the R<sup>2</sup> substituents (Table 14).<sup>26,45,85,372,374</sup> The same trend was observed for the nonliving catalysts 86–89, although the syndiospecificity was always lower than that of the

corresponding living catalysts (Table 15).<sup>163</sup> The buried volume theory proposed by Cavallo et al. is also in line with the observations.<sup>453</sup>

De Rosa and co-workers studied the microstructures of the sPP obtained with bis(phenoxy–imine) Ti complexes and their relations to the crystal structures, the crystallization behavior, and the mechanical properties in comparison to the sPP with comparable stereospecificity obtained with a C<sub>s</sub>-symmetric metallocene catalyst.<sup>471</sup> Probably due to significant amounts of the regio-irregular units in the sPP produced by the bis(phenoxy–imine) Ti complex, substantial differences were observed in the crystal structures and elastic properties.

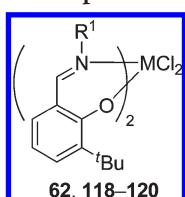
The effects of the R<sup>2</sup> substituents on the polymerization activities were investigated for the living (R<sup>1</sup> = C<sub>6</sub>F<sub>5</sub>)<sup>85</sup> and nonliving (R<sup>1</sup> = Ph)<sup>163</sup> systems. In either case, the activities were not related to the size of R<sup>2</sup> in a way previously seen for the ethylene polymerizations, where the higher activity was observed for the bulkier R<sup>2</sup>. In both living and nonliving catalysts, the complexes having R<sup>2</sup> = Me (complexes 155 and 87) exhibited the highest activities for propylene polymerization. Since propylene is much larger than ethylene, it is reasonable to assume that the bulky R<sup>2</sup> would significantly impede the coordination and insertion of the propylene monomer, which compensates for the beneficial effects of the large R<sup>2</sup>.

The complexes bearing various aryl substituents at R<sup>1</sup> (complexes 152–164) were also examined by Coates and co-workers (Table 16).<sup>162</sup> The observations were quite similar to those which were made for ethylene polymerizations; that is, (1) at least one *ortho*-fluorine at the N-aryl group enables living polymerizations; (2) the *ortho*-fluorine suppresses the activity when compared with non-*ortho*-F complexes, except for the C<sub>6</sub>F<sub>5</sub> group, which shows the highest activity; (3) electron-withdrawing groups at the 3-, 4-, or 5-positions greatly enhance the polymerization activity relative to R<sup>1</sup> = Ph; and specifically for propylene polymerization, (4) the complexes that have fluorines at the 2,4,6-positions are more syndioselective. It was also pointed out that the *ortho*-F complexes retained the C<sub>2</sub>-symmetric *cis*-N/*trans*-O/*cis*-Cl geometry in solution; however, a considerable amount of the C<sub>1</sub>-isomer was observed in solution for the others. Subsequently, the same group prepared a more diverse ligand library in R<sup>1</sup> and examined propylene polymerization characteristics, including heteroligated complexes using a pooled combinatorial method assayed by GPC.<sup>194</sup> Interestingly, they found out that certain living/nonliving ligand combinations provided the heteroligated complexes exhibiting much higher polymerization activities than both of the parent homoligated complexes. The activity enhancement was not observed for the libraries consisting of only living ligands or only nonliving ligands, where the activities appeared to fall between two parent homoligated complexes.

With regard to the *ortho*-F effects for the observed living polymerizations, Fujita and co-workers expanded the attractive interaction between the *ortho*-F and the β-H of the growing polymer chain to the propylene polymerization, which was hypothesized for the living polymerization of ethylene with the same catalysts. In fact, DFT calculations demonstrated the feasibility of the interaction for either 1,2- or 2,1-inserted species modeled by isobutyl and secondary butyl groups, respectively. The calculated distances and the electrostatic energies for these model species were similar to those for the ethylene inserted species.<sup>85</sup>

Talarico and co-workers presented a counterargument against the attractive interaction theory also based upon the

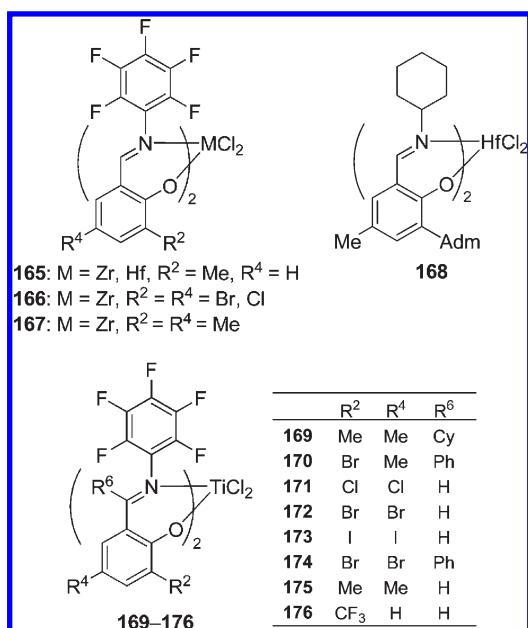
**Table 17. Propylene Polymerization Results for the Phenoxy–Imine Zr and Hf Complexes<sup>a</sup>**



complex	R <sup>1</sup>	M	activity [g-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>b</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
118	C <sub>6</sub> F <sub>5</sub>	Zr	428	1340	2.34
119	C <sub>6</sub> F <sub>5</sub>	Hf	380	9900	2.73
62	Ph	Zr	688	150	1.55
120	Ph	Hf	59	370	1.62

<sup>a</sup> Polymerization conditions: toluene 250 mL; complex, 0.1–0.5 μmol; DMAO, 1.25 mmol; propylene, 0.1 MPa; 25 °C; 5 min. <sup>b</sup> Determined by GPC (polystyrene calibration).

**Chart 12**



calculations.<sup>472–474</sup> They argued that the *ortho*-F effects could be explained by a traditional repulsive nonbonding interaction, which sterically destabilized the more encumbered transition state for β-H transfer to the coordinated propylene monomer in a 1,2-fashion more than the transition state of the 2,1-propagation, assuming β-H transfer to the coordinating monomer. Unfortunately, they could not extend these calculations to the living ethylene polymerization because they said that the elementary steps of ethylene polymerization were not well understood. Even though the conclusion about the *ortho*-F effects and the livingness must wait for another study to enhance clarification, the living bis(phenoxy–imine) Ti catalysts have provided a practical means and many opportunities to create new materials, which will be discussed in later sections (see section 10.4).

The effects of the group 4 metal center (Zr and Hf) were examined for perfluorinated and non-fluorinated N-aryl complexes by Fujita and co-workers.<sup>475</sup> In both cases, the polymerizations are not living, and chain transfer reactions are frequent, in contrast to the cases of the living or high-molecular-weight-prone Ti complexes. In general, the perfluorinated complexes gave higher molecular weight polymers than the non-fluorinated complexes, and the Hf complexes gave higher molecular weight polymers than the Zr complexes (Table 17). The analysis of the chain-end structures obtained with these catalysts (62 and 118) revealed two consecutive 1,2-insertions for the initiating chain ends as well as various unsaturated chain ends indicative of β-H transfer, mostly after 2,1-insertion. For the Hf complexes, chain transfer to MAO (or rather to concomitant AlMe<sub>3</sub>) occurred to an appreciable degree, especially at higher polymerization temperatures. The stereochemistry was virtually atactic or slightly syndiotactic, and the regiochemistry appeared to be in a 1,2-fashion but with considerable regioerrors.

Polymerizations with bis(phenoxy–imine) Zr complex 165, bearing R<sup>2</sup> = CH<sub>3</sub>, were also examined by Pellecchia and co-workers (Chart 12).<sup>219,462</sup> The chain end analysis of the polymers revealed that the isobutyl group and vinylidene were in about a 10/1 molar ratio, which suggested that the polymerizations were mediated prevailingly via a 1,2-insertion mode, and most of the polymer chains were terminated through chain transfer to MAO (or rather to concomitant AlMe<sub>3</sub>). The polymers were prevailingly syndiotactic (*rr* ~ 44%), which follows the chain-end-control statistics. Copolymerization of propylene and a small amount of <sup>13</sup>C-enriched ethylene further demonstrated the prevailing 1,2-regiochemistry because most of the ethylene was found in the three consecutive methylene sequences (79%). They also found that the syndioselectivity after the ethylene unit was somewhat lower (*r* = 58%) than that of the consecutive propylene units (*r* = 67%) and in agreement with the expectation for the chain-end-controlled nature. Zirconium complexes 166 having R<sup>2</sup> = R<sup>4</sup> = Br and Cl were beneficial to the activity and exhibited higher 1,2-insertion regioselectivity but slightly lower syndiospecificity in comparison with complex 167, which has R<sup>2</sup> = R<sup>4</sup> = Me.<sup>422</sup> These complexes can polymerize 1-hexene into low molecular weight atactic regioregular polymers.

Grassi and co-workers demonstrated that some bridged tetradentate diimino-bisphenolate Zr complexes exhibited 1,2-insertion regiochemistry of a higher level than bis(phenoxy–imine) Zr complexes.<sup>42</sup>

The opposite regiochemistry of Ti and Zr/Hf was discussed by means of calculations in the literature described above.<sup>463–466</sup>

**4.1.2.2. Isotactic Polypropylene.** By using the <sup>i</sup>Bu<sub>3</sub>Al/Ph<sub>3</sub>-CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> activation method, where the imine donors were supposed to be reduced into the amine donors of the type –CH<sub>2</sub>N(R<sup>1</sup>)Al<sup>i</sup>Bu<sub>2</sub>, the stereospecificity was found to be altered dramatically. Fujita and co-workers demonstrated that when activated with <sup>i</sup>Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, Zr and Hf complexes exhibited isospecificity via an enantiomorphic site-control mechanism, while the corresponding Ti complex afforded nearly completely atactic but extremely high molecular weight (M<sub>w</sub>, 8.3 × 10<sup>6</sup> g/mol) polypropylene under the same conditions (mm, Ti: 22.9%; Zr: 45.8%; Hf: 69.0%).<sup>24,235,374,408</sup> After optimization of the ligand structures, the isospecificity of the boiling hexane insoluble parts reached *mmmm* 96.9–96.8% for Zr and Hf complexes 83 and 168, although the single-site characteristics were lost in these examples.<sup>26,373,476</sup> The low molecular weight sample prepared in the presence of H<sub>2</sub> gave *n*-propyl

(46%), isobutyl (47%), and *n*-butyl (6%) chain ends, which implied that the polymerizations were mediated by successive 1,2-insertions on the assumption that the dormant species caused by occasional regioerrors were reactivated by hydrogenation.

The origin of the isospecificity is unclear, but it is not impossible to assume a  $C_2$ -symmetric structure of these bis(phenoxy–amine) octahedral complexes, where the site isomerization discussed above may be slow, or a  $C_1$ -symmetric structure resulted by dissociation of one of the amine donors.<sup>7,9,12,364</sup>

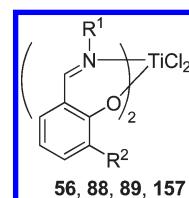
Coates and co-workers revealed that *N*-fluoroaryl bis(phenoxy–ketimine) Ti complexes performed moderately isoselective living propylene polymerization (*mmmm* 73%). The stereoerrors found in the iPP suggested a site-control mechanism for the polymerization. Regarding the regiochemistry, 2,1-insertion was tentatively suggested from the results of cyclopolymerization of  $\alpha,\omega$ -diene.<sup>90,91</sup> Complex **169**, bearing a cyclohexyl group as R<sup>6</sup>, afforded the highest isospecificity of *mmmm* 73% ( $T_m$  116.8 °C) at 0 °C polymerization. The observed isospecificity was believed to be due to bulky R<sup>6</sup> substituents, which would make the fluxional  $\Delta/\Delta$  isomerization prohibitive or slow relative to propagation.

Mazzeo and co-workers reported that bis(phenoxy–imine) Ti complexes **171**–**174**, bearing I, Br, Cl, as R<sup>2</sup> (and R<sup>4</sup>) substituents, afforded prevailingly isotactic PPs via an enantiomeric site control mechanism in a nonliving fashion (**173**: *mm* 73% at –20 °C).<sup>94</sup> The polymerization activity increased in the order **171** > **172** > **173** (Cl > Br > I), but the isospecificity increased in the opposite order, **173** > **172** > **171** (I > Br > Cl). The intensive microstructural analyses of the polymers revealed a regioblock structure consisting of short isotactic blocks and longer poorly isotactic blocks. To elucidate the origin of the isospecificity, they examined a phenoxy–ketimine complex **174** (R<sup>2</sup> = R<sup>4</sup> = Br, R<sup>6</sup> = Ph), which was not stereospecific in propylene polymerizations despite apparent similarity to the complexes examined by Coates' group<sup>91</sup> (for example, **170**: R<sup>2</sup> = Br, R<sup>4</sup> = CH<sub>3</sub>, R<sup>6</sup> = Ph; *mmmm* 57% at 0 °C). In addition, the phenoxy–imine complex **175** that bears methyl groups at R<sup>2</sup> and R<sup>4</sup> was also aspecific despite the nearly equivalent size of the methyl and bromine. Therefore, electron-withdrawing groups at particular positions appeared to be important for the observed isospecificity. In fact, it was reported that complex **176** (R<sup>2</sup> = CF<sub>3</sub>) also provided iPP via a site-control mechanism.<sup>373</sup>

The Zr congeners (**166**, R<sup>2</sup> = R<sup>4</sup> = Br, Cl) afforded a stereo-irregular, slightly syndiotactic enriched (*mm* 13%) PP having relatively low molecular weights via highly regular 1,2-enchainment.<sup>222</sup> When compared with the complex that has a methyl group as R<sup>2</sup> (**167**), these halogenated complexes are considerably higher in activity and in regiospecificity.

**4.1.2.3. Polymerization of Higher  $\alpha$ -Olefins.** Fujita and co-workers demonstrated that, upon activation with  $^t\text{Bu}_3\text{Al}$  and Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, a Ti complex **88** polymerized 1-hexene into extremely high molecular weight ( $10^5$ – $10^6$  g/mol) atactic poly(1-hexene)s with significant regioerrors (~50 mol %).<sup>24,26,46,408,477</sup> The narrow PDI values (<2.0) are indicative of single site polymerization behaviors, whereas the same complex was shown to be virtually inactive toward 1-hexene when activated with MAO or when the polymerizations were carried out in toluene instead of *n*-heptane. This catalyst was further revealed to show unique polymerization characteristics to higher  $\alpha$ -olefins. First, the activities became higher in the order, 4-methyl-1-pentene > 1-decene > 1-octene > 1-hexene when compared with a typical

**Table 18. Effects of the Substituents of the Phenoxy–Imine Ti Complexes on Styrene Polymerization Behavior<sup>a,b</sup>**



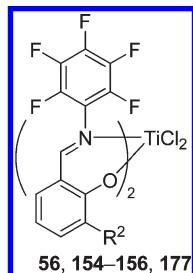
complex	R <sup>1</sup>	R <sup>2</sup>	activity					tacticity <sup>e</sup>
			[g-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>c</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	T <sub>m</sub> <sup>d</sup> (°C)		
88	Ph	<sup>t</sup> Bu	0.56	215	7.5	275	syn	
88 <sup>f</sup>	Ph	<sup>t</sup> Bu	0.12	779	2.4	275	syn	
89	Ph	TMS	0.64	132	9.0	279	syn	
56	C <sub>6</sub> F <sub>5</sub>	<sup>t</sup> Bu	5.21	10	4.4	224	iso	
157	C <sub>6</sub> F <sub>5</sub>	TMS	10.15	8	2.3	213	iso	
157 <sup>f</sup>	C <sub>6</sub> F <sub>5</sub>	TMS	1.37	10	2.4	217	iso	

<sup>a</sup> Polymerization conditions: toluene, 30 mL; styrene, 100 mL; complex, 0.2 mmol; DMAO, 50 mmol; 20 °C; 60 min. <sup>b</sup> Results are based on methyl ethyl ketone-insoluble polymers. <sup>c</sup> Determined by GPC (polystyrene calibration). <sup>d</sup> Determined by DSC. <sup>e</sup> Determined by <sup>13</sup>C NMR (syn, syndiotactic; iso, isotactic). <sup>f</sup> 0 °C, 360 min.

*ansa*-metallocene, *rac*-(C<sub>2</sub>H<sub>4</sub>)(1-indenyl)<sub>2</sub>ZrCl<sub>2</sub>, which showed the completely opposite order of the activities, which intuitively makes more sense.<sup>46,401,402</sup> The molecular structures of all the poly( $\alpha$ -olefin)s obtained by **88** were random in terms of stereo- and regiochemistry and had very high molecular weights. Moreover, the polymerization rate and the polymer molecular weights exhibited a zeroth order dependence on the concentration of 1-hexene. DFT calculations on the assumed phenoxy–amine species that bears  $-\text{CH}_2\text{N}(\text{Ph})(^t\text{Bu}_2\text{Al})$  as the N donor suggested the extremely labile nature of the amine donors. The methyl cationic species takes a trigonal bipyramidal geometry with two oxygens trans to each other. Upon coordination of 1-hexene, one of the N donors was dissociated from the Ti metal, and the species looked alike, taking a square pyramidal geometry with the Ti-bound methyl at the apical site. The detached N donor appeared to be out of the coordination sphere during the transition state of insertion, too. This means that 1-alkene and probably toluene are much better donors than the  $-\text{CH}_2\text{N}(\text{Ph})(^t\text{Bu}_2\text{Al})$ . The strong coordination of toluene may cause the observed inactivity in toluene. The labile nature of the N donor is the key to explaining the activity dependence on the monomer size and the independence of the monomer concentration. The larger monomer and therefore sterically encumbered polymer chains will enhance the N donor dissociation, which makes the active species sterically more open and more electrophilic and thus accelerates the polymerizations. The zeroth order kinetics might be attributed either to a stable olefin coordinated species or to the N coordinating (olefin noncoordinating) species as a resting state. The olefin insertion or the dissociation of the N donor will be the rate determining step in each case.

The *N*-perfluoroaryl bis(phenoxy–imine) Zr complexes **166** bearing Br or Cl as R<sup>2</sup> and R<sup>4</sup> substituents were applied to 1-hexene polymerizations, giving low molecular weight, low stereospecific polymers, but again with relatively high regiospecificity in a similar way as that observed for propylene polymerizations with these complexes.<sup>222</sup> The activation with  $^t\text{Bu}_3\text{Al}$  and

**Table 19. Effects of the R<sup>2</sup> Substituents of the Phenoxy–Imine Ti Complexes on Ethylene Polymerization and Ethylene/1-Hexene Copolymerization Behavior<sup>a,b</sup>**



complex	R <sup>2</sup>	comonomer	activity [g-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>c</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	comonomer content <sup>d</sup> (mol %)
<b>56</b>	<sup>t</sup> Bu		34.0	412	1.13	
		1-hexene	0.80	54.5	1.19	3.2
<b>177</b>	Cy		3.50	49	1.05	
		1-hexene	0.83	49.0	1.14	12.0
<b>156</b>	<sup>i</sup> Pr		3.88	51	1.10	
		1-hexene	1.57	82.5	1.12	12.6
<b>155</b>	Me		5.65	75	1.16	
		1-hexene	1.80	102	1.12	17.7
<b>154</b>	H		2.53	44	1.08	
		1-hexene	1.01	54.2	1.07	22.6

<sup>a</sup> Ethylene polymerization conditions: toluene, 250 mL; complex **56**, 0.5 μmol; complexes **154–177**, 5 μmol; MAO, 1.25 mmol; ethylene, 100 L/h; 25 °C; 1 min. <sup>b</sup> Copolymerization conditions: toluene, 200 mL; complex, 2.5 mmol; ethylene, 100 L/h; 1-hexene, 50 mL; 25 °C; 5 min. <sup>c</sup> Determined by GPC (polyethylene calibration). <sup>d</sup> Determined by <sup>1</sup>H NMR.

Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> afforded poly(1-hexene) with slightly higher molecular weight but with a similar stereoirregularity.

#### 4.1.2.4. Polymerization of Styrene and Other Monomers.

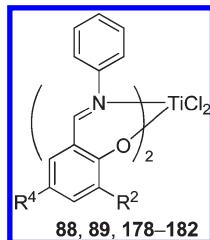
Fujita and co-workers investigated styrene polymerization using bis(phenoxy–imine) Ti complexes **56**, **88**, **89**, and **157**, where the R<sup>1</sup> substituent caused a drastic change of stereospecificity (Table 18).<sup>478</sup> At 20 °C, the non-fluorinated complexes (R<sup>1</sup> = Ph) afforded syndiotactic polystyrene (sPS), while isotactic polystyrene (iPS) was obtained from the fluorinated complexes (R<sup>1</sup> = C<sub>6</sub>F<sub>5</sub>). The obtained sPS and iPS had virtually no stereoerrors and showed high melting transition temperatures (*T<sub>m</sub>* ~ 270 °C for sPS, ~220 °C for iPS), which are consistent with the reported values. The active species for the sPS formation were attributed to the Ti(III) species generated by the ligand transfer reaction from an initially formed cationic species, [(L<sup>Fl</sup>)<sub>2</sub>Ti<sup>IV</sup>Me]<sup>+</sup>, to Me<sub>3</sub>Al included in MAO, as discussed in section 3.4. This assumption is rational considering the polymerization mechanism generally accepted for typical syndiospecific styrene polymerization catalysts such as CpTiX<sub>3</sub>.<sup>479</sup> The cationic Ti(IV) species derived from the non-fluorinated complexes appeared to be inactive to styrene polymerization and decomposed into Ti(III) species, which were active toward syndiospecific styrene polymerization. Meanwhile, the fluorinated versions of cationic [(L<sup>Fl</sup>)<sub>2</sub>TiMe]<sup>+</sup> species were active toward styrene polymerization, probably due to the higher electrophilicity derived from the C<sub>6</sub>F<sub>5</sub> group, and the decomposition to Ti(III) was suppressed during the polymerization, at least below 20 °C. Higher polymerization temperature or pretreatment of the complexes with MAO accelerated the decomposition, and therefore, the yields of sPS were increased for the fluorinated complexes and mixtures of iPS and sPS were obtained.

The observed isospecificity is apparently justifiable, considering *C*<sub>2</sub>-symmetric structures of the cationic [(L<sup>Fl</sup>)<sub>2</sub>Ti–Me]<sup>+</sup> species, although lack of any stereoerrors in the polymers prevented an actual proof of the stereoregulating mechanisms.

Pellecchia and co-workers investigated the polymerization of conjugated dienes using bis(phenoxy–imine)Ti complexes with MAO. At the ambient temperatures or lower, the polymers consisting of 1,4-cis enchainments were obtained from 1,3-butadiene, isoprene, and (Z)-1,3-pentadiene, while (E)-1,3-pentadiene gave a mixture of 1,4-cis/trans polymers at a higher rate than (Z)-1,3-pentadiene, and 4-methyl-1,3-pentadiene afforded 1,2-enchained polymer.<sup>480</sup> Partial removal of the phenoxy–imine ligands was suggested for the observed stereoselectivity. Fujita and co-workers also reported on the polymerization of 1,3-butadiene with bis(phenoxy–imine)Ti complexes.<sup>26</sup>

Masuda and co-workers carried out the polymerization of vinyl ethers with bis(phenoxy–imine) group 4 metal complexes.<sup>481</sup> The polymerizations were suggested to proceed via a carbocationic mechanism.

4.1.3. Copolymerization. Despite a fairly few number of constituting olefin monomers, the relative ease of copolymerization between these olefinic monomers allows the polyolefin products to exhibit an extremely wide range of physical and mechanical properties. To meet this end, however, judicious choice and fine-tuning of catalyst are often required. In this section, copolymerizations of ethylene with various comonomers using bis(phenoxy–imine) group 4 metal complexes are discussed, with an emphasis on the relationship between the molecular structure of the catalyst and comonomer uptake and copolymerization activities.

**Table 20.** Effects of the Substituents of the Phenoxy–Imine Ti Complexes on Ethylene/Propylene Copolymerization Behavior<sup>a</sup>

complex	R <sup>2</sup>	R <sup>4</sup>	yield (g)	activity [kg-polymer/ (mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	propylene content <sup>c</sup> (mol %)
178	'Pr	H	0.147	0.18	20.4	1.30	26.4
179	Cy	H	0.380	0.45	57.3	1.36	26.0
180	cyclooctyl	Me	0.728	0.88	83.2	1.65	26.2
181	cyclododecyl	Me	0.911	1.09	78.2	1.72	25.5
88	'Bu	H	0.541	0.68	69.1	1.88	6.3
182	CMe <sub>2</sub> Ph	Me	0.320	0.38	12.7	1.95	4.2
90	Ph	H	2.93	3.42	42.1	1.82	38.8

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 5.0 μmol; DMAO, 1.25 mmol; ethylene feed, 50 L/h; propylene feed, 150 L/h; 50 °C; 10 min.

<sup>b</sup> Determined by GPC (polyethylene calibration).

<sup>c</sup> Determined by IR.

**4.1.3.1. Ethylene with α-Olefins (Including Styrene).** In the living polymerization with *N*-perfluorinated aryl Ti complexes (**56**, **154–156**, **177**), the effects of R<sup>2</sup> substituents were investigated by Fujita and co-workers (Table 19).<sup>373,407</sup> As mentioned in section 4.1.1.1, complex **56** (R<sup>2</sup> = <sup>t</sup>Bu) exhibited far higher activity (6–13×) than the others (R<sup>2</sup> = cyclohexyl, <sup>i</sup>Pr, Me, H) in ethylene homopolymerization. However, in the copolymerization of ethylene with 1-hexene, the activities became much lower and similar to each other (0.8–1.8 g-polymer/(mmol·M·h)), but all the (co)polymerizations exhibited a typical living behavior, as exemplified by very small PDI values (<1.2). Under the conditions examined, the comonomer uptake follows the order of the size of R<sup>2</sup> (H > Me > <sup>i</sup>Pr ~ cyclohexyl ≫ <sup>t</sup>Bu). The same trend was observed for 1-octene and 1-decene copolymerizations, although the comonomer uptakes were slightly reduced from C<sub>6</sub> to C<sub>8</sub> to C<sub>10</sub> olefins. Clearly, steric effects between R<sup>2</sup> and the comonomers are at work in these examples, which is reasonable because the R<sup>2</sup> substituents are situated above and below the reaction sites (see section 3.1.1). Fan, Xu, and their co-workers prepared a series of poly(ethylene-*co*-propylene) (EPR) using living catalyst **56** and confirmed a narrow and uniform distribution of propylene monomers by thermal fractionation.<sup>482–484</sup> Furthermore, Coates and co-workers investigated the rheological behavior of the EPR prepared by living catalyst **152**, which demonstrated that the syndiotactic propylene units in the copolymer increased the plateau modulus, the unperturbed chain dimension, and the entanglement molecular weights relative to iPP or aPP units in EPR, as indicated for the propylene homopolymers.<sup>485</sup>

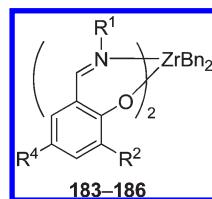
The R<sup>2</sup> effects were also investigated for non-fluorinated Ti catalysts (R<sup>1</sup> = Ph) (Table 20).<sup>83</sup> In ethylene/propylene copolymerizations, propylene uptake was almost constant (~26 mol %) for complexes **178–181** with secondary alkyl R<sup>2</sup> (<sup>i</sup>Pr, cyclohexyl, cyclooctyl, cyclododecyl), which was much higher than tertiary alkyl R<sup>2</sup> (**88**, 6.3 mol %; **182**, CMe<sub>2</sub>Ph, 4.2 mol %). On the other hand, the activities among the secondary alkyl R<sup>2</sup> became higher depending on the ring size, i.e., cyclododecyl > cyclooctyl > (<sup>t</sup>Bu) > cyclohexyl > <sup>i</sup>Pr, which is generally

consistent with the observations made for ethylene homopolymerization (see section 4.1.1.1). It should be noted that the complexes bearing cyclooctyl and cyclododecyl as R<sup>2</sup> substituents demonstrated higher activity than the complex having tertiary alkyl R<sup>2</sup> (= <sup>t</sup>Bu). What is more interesting is that complex **90** having R<sup>2</sup> = Ph established significantly higher activity and higher propylene uptake than any of the other complexes. As a measure of the steric congestion around the titanium, the distances between chlorine and the nearest carbon in the ligands were estimated from the solid state structures of the catalyst precursors (dichlorides). According to these distances, the steric congestion is supposed to be large in the order of Ph > <sup>t</sup>Bu > cyclohexyl > cyclooctyl, which is inconsistent with the observed comonomer uptake. The DFT calculations on ethylene-coordinated cationic species bearing a Ti-bound *n*-propyl group suggested that the phenyl group can easily release the steric constraints by rotation due to its planar nature.

These catalysts behave somewhat differently in copolymerization of ethylene with higher α-olefins. The comonomer uptake becomes larger in the order of cyclododecyl ≥ Ph > cyclooctyl > cyclohexyl ≫ <sup>t</sup>Bu for both 1-hexene and 1-decene. However, the activities follow the order of Ph ≫ cyclododecyl > cyclooctyl > cyclohexyl ≫ <sup>t</sup>Bu. Therefore, a subtle steric balance between R<sup>2</sup> substituents, coordinating substrates (olefins, R<sub>3</sub>Al, counteranion, etc.) and metal-bound growing polymer chains seems to determine the comonomer uptake and the activity. The R<sup>2</sup> substituents in appropriate size will allow a large comonomer molecule to coordinate to the metal but can sterically prevent the deactivation pathways by protecting the reaction site (see section 3.4) or efficiently destabilize the active species in its resting state.

The R<sup>2</sup> substituents in bis(phenoxy-imine) Zr complexes also demonstrated decisive effects on comonomer uptake in ethylene/propylene copolymerization in a similar way.<sup>486</sup> The monomer reactivity ratios were estimated for complexes **183–186** using the Fineman–Ross method (Table 21), where the r<sub>1</sub> values represent the relative reactivity of ethylene to propylene (ethylene selectivity) toward the ethylene last inserted species,

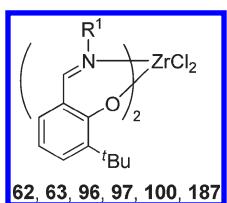
**Table 21. Effects of the Substituents of the Phenoxy–Imine Zr Complexes on Monomer Reactivity Ratios in Ethylene/Propylene Copolymerizations<sup>a</sup>**



complex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	propylene in feed <sup>b</sup> (mol %)	propylene conversion (%)	propylene content <sup>c</sup> (mol %)	r <sub>1</sub>
183	2-methylcyclohexyl	cyclooctyl	Me	32.25	8.6	2.39	16
184	Ph	<sup>t</sup> Bu	H	58.84	7.6	2.59	45
185	2-methylcyclohexyl	<sup>t</sup> Bu	Me	58.84	7.7	1.79	69
186	2-methylcyclohexyl	cumyl	Me	58.84	0.42	0.88	152

<sup>a</sup> Polymerization conditions: hexane, 5.0 mL; Al(DMAO)/Zr = 300; 100 °C; 10 min; 0.7 MPa gauge pressure maintained by continuous ethylene supply.  
<sup>b</sup> Calculated initial monomer composition. <sup>c</sup> Determined either by IR or <sup>13</sup>C NMR.

**Table 22. Effects of the R<sup>1</sup> Substituents of the Phenoxy–Imine Zr Complexes on Ethylene/Propylene Copolymerization Behavior<sup>a</sup>**



complex	R <sup>1</sup>	activity [kg-polymer/(mmol-M·h)]	propylene content <sup>b</sup> (mol %)
63	Cy	4.63	12.1
62	Ph	10.1	29.2
96	2-MeC <sub>6</sub> H <sub>4</sub>	2.3	3.09
187	4-MeC <sub>6</sub> H <sub>4</sub>	5.14	26.3
97	2-PrC <sub>6</sub> H <sub>4</sub>	4.25	6.5
100	3,5- <sup>t</sup> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	5.41	14.5

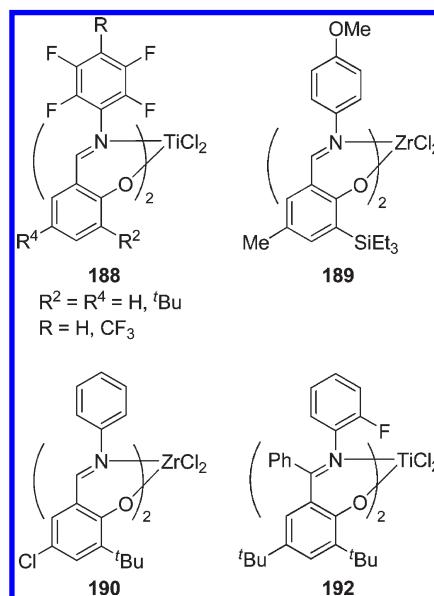
<sup>a</sup> Polymerization conditions: toluene, 250 mL; catalyst, 5 μmol; MAO, 1.25 mmol; ethylene, 50 L/h; propylene, 150 L/h; 25 °C; 15 min.

<sup>b</sup> Determined by IR.

(L<sup>FI</sup>)<sub>2</sub>Zr–CH<sub>2</sub>CH<sub>2</sub>–R (monomer 1 = ethylene, monomer 2 = propylene). The r<sub>1</sub> for complex 183 bearing cyclooctyl groups as R<sup>2</sup> is 16, meaning that ethylene is 16 times more reactive than propylene in this copolymerization at 100 °C. Likewise, complexes 184 and 185 that have <sup>t</sup>Bu groups as R<sup>2</sup> show much higher ethylene selectivity, i.e., r<sub>1</sub> = 45 and 69. The difference between 184 and 185 could be brought by R<sup>1</sup>, Ph vs 2-methylcyclohexyl. A similar observation was made in the patent application by Mitsui Chemicals in 1997.<sup>19</sup> In a series of ring-substituted N-aryl bis(phenoxy–imine) Zr complexes 63, 62, 96, 187, 97, and 100, alkyl substitution at an ortho-position significantly reduced propylene uptake in the copolymers in ethylene/propylene copolymerizations (Table 22).

The ethylene selectivity of the CMe<sub>2</sub>Ph group as R<sup>2</sup> becomes extremely high at r<sub>1</sub> = 152, despite the difference of only one carbon in the substrates and high polymerization temperature at

**Chart 13**



100 °C. To elucidate the origin of the selectivity, DFT calculations were carried out on the transition states of ethylene or propylene insertion to the cationic (L<sup>FI</sup>)<sub>2</sub>Zr–CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> species. The computed structures clearly showed that the selection was made based on the size and shape of the reaction sites, which was just right for ethylene but too small for propylene, working like a molecular zeolite.

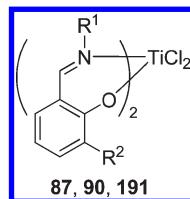
The highly ethylene selective nature of the bis(phenoxy–imine) Zr catalysts in combination with the chain-shuttling capability was ingeniously applied to the preparation of multi-block copolymers by the scientists at The Dow Chemical Company (see section 10.4).

Bulychev and co-workers reported that addition of 1-hexene (1.1–2.2 equiv to ethylene) might improve the stability of the active species derived from complexes 188 (Chart 13).<sup>199,200</sup> During the polymerizations, the steady kinetic profiles were

**Table 23. Effects of the Cocatalyst on Ethylene/Propylene Copolymerization Behavior Catalyzed by the Phenoxy–Imine Zr Complex<sup>a</sup>**

complex	cocatalyst (amount [mmol])	yield (g)	activity [kg-polymer/ (mmol·M·h)]	$M_v$ (kg/mol)	$M_w/M_n^b$	propylene content <sup>c</sup> (mol %)
62	MAO (1.25)	4.66	22	5	2.45	10.1
62	<sup>i</sup> Bu <sub>3</sub> Al/Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> (0.275/0.005)	1.63	8	1090	1.83	20.7

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 2.5  $\mu$ mol; ethylene, 100 L/h; propylene, 100 L/h; 50 °C; 5 min. <sup>b</sup> Determined by GPC (polystyrene calibration). <sup>c</sup> Determined by IR.

**Table 24. Results of Ethylene/NBE Copolymerization with the Phenoxy–Imine Ti and Typical Metallocene-Based Complexes<sup>a</sup>**

complex	R <sup>1</sup>	R <sup>2</sup>	activity [kg-polymer/ (mmol·M·h)]	NBE content <sup>b</sup> (mol %)	T <sub>g</sub> <sup>c</sup> (°C)	$M_w^d$ (kg/mol)	$M_w/M_n^d$
87	Ph	Me	0.65	48.7	120	186	1.09
90	Ph	Ph	3.27	45.7	120	573	1.21
191 <sup>e</sup>	pyrrolyl	Ph	6.98	46.1	126	215	1.91
CGC <sup>f</sup>			4.80	25.8	47	2330	3.19
<i>rac</i> -(C <sub>2</sub> H <sub>4</sub> )(1-indenyl) <sub>2</sub> ZrCl <sub>2</sub>			1.75	27.7	49	476	1.74
Me <sub>2</sub> C(9-fluorenyl)(Cp)ZrCl <sub>2</sub>			1.40	28.0	49	259	1.58

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 1.0  $\mu$ mol; charged norbornene, 5 g; ethylene, 0.1 MPa; cocatalyst DMAO, 1.25 mmol as Al; 25 °C; 10 min. <sup>b</sup> Determined by <sup>13</sup>C NMR. <sup>c</sup> Measured by DSC. <sup>d</sup> Determined by GPC (polystyrene calibration). <sup>e</sup> Complex 0.5  $\mu$ mol. <sup>f</sup> Polymerization time 5 min; cocatalyst Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> 6  $\mu$ mol; <sup>i</sup>Bu<sub>3</sub>Al 0.25 mmol.

observed in the presence of 1-hexene in contrast to rather rapid activity decay for ethylene homopolymerization, although it may be explained in terms of improved mass diffusion due to the polymers becoming more soluble.

The bis(phenoxy–amine) ligated species, which are generated *in situ* by activating (L<sup>FI</sup>)<sub>2</sub>MX<sub>2</sub> with <sup>i</sup>Bu<sub>3</sub>Al and Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, exhibit in general high molecular weight capability (section 3.2.1), unusual regio- and stereoselectivity (section 4.1.2), and also higher comonomer incorporation relative to the original bis(phenoxy–imine) ligated species. For example, the comparison of activation method was compiled in Table 23 for Zr complex 62 in ethylene/propylene copolymerization.<sup>205</sup> MAO activation afforded low molecular weight ( $M_v$ , 5000 g/mol) EPR at the efficiency of 22 kg-polymer/(mmol·M·h). The activation with <sup>i</sup>Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, on the other hand, provided much higher molecular weight EPR ( $M_v$ , 1,090,000 g/mol) at lower activity (8 kg-polymer/(mmol·M·h)). The propylene contents were 10.1 mol % for the former and 20.7 mol % for the latter, indicating a significant enhancement of comonomer uptake for the bis(phenoxy–amine) ligated species. To this end, appropriate ligand modification led to complex 189, which produced ultrahigh molecular weight EPR (propylene 23.7 mol %,  $M_w \sim 10^7$  g/mol) via a single site mechanism (PDI 2.52).<sup>26,46,215,408</sup>

The heteroligated (phenoxy–imine)(pyrrolyl–imine) complexes developed by Lancaster, Bochmann, and co-workers (see section 4.1.1.5) were examined for ethylene/1-hexene and ethylene/propylene copolymerizations.<sup>308,346</sup> The heteroligated

Ti complex appeared to inherit a good part of each homoligated parent complex, exhibiting superior polymerization characteristics in activity, comonomer uptake, and molecular weight. The monomer reactivity ratios ( $r_1$ , monomer 1 = ethylene) were estimated for ethylene/propylene copolymerizations, which insignificantly varied from 15 to 50 depending on the N-alkyl groups in pyrrolyl–imine ligands.

Qian and co-workers prepared some hybrid complexes bearing phenoxy–imine and cyclopentadienyl ligands and examined olefin polymerizations. The mixed ligand complex 150 exhibited comparable to better performances relative to Cp<sub>2</sub>TiCl<sub>2</sub> or (L<sup>FI</sup>)<sub>2</sub>TiCl<sub>2</sub>.<sup>104</sup>

Finally, Scott and co-workers made an interesting discovery in the copolymerization of ethylene and styrene.<sup>223</sup> The complexes 62, 133, and 190 demonstrated a sluggish activity for copolymerization of ethylene and styrene and afforded a mixture of homopolymers, i.e., low molecular weight PE and higher molecular weight atactic polystyrene. By changing the comonomer to 4-*tert*-butylstyrene (TBS), the copolymerization turned to exhibit a steady kinetic profile and high activity, comparable to those of ethylene homopolymerization. The obtained polymers showed no sign of molecular weight reduction vs ethylene homopolymers and narrow molecular weight distributions (PDI 1.9–2.8), having 5–11 mol % of TBS contents. DFT calculations dismissed the possibility of steric interaction at any stage of the TBS insertion. The following hypotheses were given as possible rationales that TBS (1) prefers 1,2-insertion over 2,1-insertion, which would generate a low reactive benzyl species, or

(2) electronically activates the 2,1-inserted benzyl species, which would otherwise serve as a dormant species. By sequential monomer addition, Weiser and co-workers prepared styrenic block copolymers with concurrent formation of atactic polystyrene homopolymers using a living bis(phenoxy-imine) Ti complex (see Table 26).<sup>487,488</sup>

Ethylene/1,3-butadiene copolymerization with a bis(phenoxy-imine) complex/MAO gave copolymers that had mostly 1,2- or 1,4-insertion units (96%) with a small amount of 1,2-cyclopentane units (4%).<sup>26</sup>

**4.1.3.2. Ethylene with Cyclic Olefins.** Cyclic olefin copolymers (COC) generally possess high glass-transition temperature ( $T_g$ ), high optical clarity, and low birefringence due to the incorporated cyclic olefin component, and they are light in weight, high in stability to acids and alkalis, and high in moisture barrier properties. Therefore, COC products are extensively applied to food and pharmaceutical packaging, medical appliances, and production of plastic lenses and optical storage media. Because cyclic olefins used for the COC production are mostly bicyclic olefins, which are sterically encumbered and more nucleophilic than ethylene or  $\alpha$ -olefins due to their ring strain, the catalysts involved are generally required to be sterically wide open and also to be highly electrophilic at the metal center.

Fujita and co-workers revealed that sterically more open bis(pyrrolyl-imine) Ti complexes exhibited a more adaptive nature toward NBE copolymerization when compared with a prototypical bis(phenoxy-imine) Ti complex 88.<sup>489</sup> It is, however, interesting to note that the comonomer uptake of 88 is still appreciably high (vs  $Cp_2TiCl_2$ ) and also that the copolymer possesses a very narrow molecular weight distribution (PDI 1.14) indicative of a living copolymerization. Their subsequent research revealed that the close relationship between  $R^2$  substituents and comonomer uptake could also be applied to the copolymerization of ethylene and cyclic olefins (Table 24).<sup>168</sup> Under the conditions examined, complexes 178, 88, and 182 bearing  $^3Pr$ ,  $^3Bu$ , and  $CMe_2Ph$  as  $R^2$  were inactive in the presence of NBE (at 5 times higher [NBE] than those for the experiments mentioned above). However, a smaller Me group as  $R^2$  (complex 87) set off the copolymerization at 0.64 kg-polymer/(mmol-M·h), affording the copolymer with a high NBE content (48.7 mol %) and a small PDI (1.09). Moreover, the above-mentioned 90 having  $R^2 = Ph$  demonstrated much higher activity (3.27 kg-polymer/(mmol-M·h)) at a comparable NBE incorporation (45.7 mol %), while the PDI value was kept small (1.21). Complex 191, bearing  $R^1 = pyrrolyl$  and  $R^2 = Ph$ , showed even higher activity (6.98 kg-polymer/(mmol-M·h), NBE 46.1 mol %) although PDI became ~2. The calculations suggested that the observed effects of  $R^1$  were steric in nature. The living nature of 90/MAO was further confirmed by establishing a linear relationship of polymer yields and  $M_n$ , while keeping PDI ~1 all the time. It is considered that, in addition to the intrinsic living nature of bis(phenoxy-imine) Ti complexes, the NBE last-inserted species will be inherently resistant to  $\beta$ -H transfer and also that the ethylene last-inserted species might be protected by the coordination of highly nucleophilic NBE before any possible terminations can occur. The comonomer distributions are nearly alternating due to preferential coordination of more nucleophilic NBE and the prohibitively slow NBE homopropagation.<sup>52,53</sup> These NBE incorporations demonstrated by bis(phenoxy-imine) Ti catalysts are much higher (>1.7 times) than those of representative metallocenes ( $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$

(CGC), *rac*-( $C_2H_4$ )(1-indenyl) $_2ZrCl_2$ , and  $Me_2C(9\text{-fluorenyl})(Cp)ZrCl_2$ ) under the same conditions.

Coates and co-workers reported ethylene/cyclopentene copolymerization using a living bis(phenoxy-imine) Ti complex/MAO, where nearly alternating and high cyclopentene incorporating (up to 47 mol %) atactic copolymers were obtained via almost exclusive 1,2-enchainments.<sup>490</sup> They also successfully synthesized di- and triblock copolymers (Table 26).

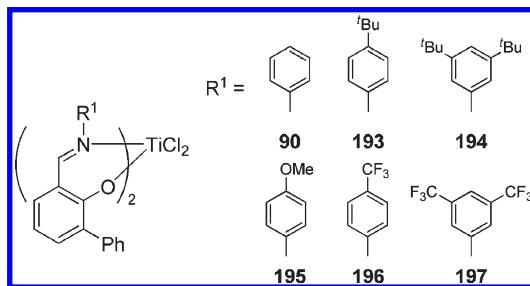
The heteroligated (phenoxy-imine)(pyrrolyl-imine) Ti complex was shown to demonstrate fairly good incorporation of NBE or cyclopentene in copolymerization with ethylene.<sup>308</sup> The heteroligated (phenoxy-imine)( $\beta$ -ketoimine) Ti complexes prepared by Li and co-workers (see section 4.1.1.5) are another example that is capable of living ethylene/NBE copolymerization at a higher range of NBE concentration (>0.4 M) in the reaction media.<sup>348</sup> Since no NBE-NBE sequences were detected in the copolymers, the living polymerization appeared to be taking place in a similar mechanism to that for the bis(phenoxy-imine) Ti complexes mentioned above.

**4.1.3.3. Ethylene with Polar Functional Olefins.** One of the grand challenges for the metal-catalyzed olefin polymerization has been copolymerization of nonpolar olefins with polar functional olefins. The copolymerization possesses the potential to provide a useful tool to control surface, interfacial, and bulk properties of unless otherwise nonpolar olefinic materials by willfully designing copolymer architectures that have specific functions at specific positions, which have been unattainable by other means such as traditional radical polymerizations or postpolymerization radical grafting.

In late-metal catalyzed olefin polymerizations, remarkable progress in this field has recently been made thanks to the understanding of active species and polymerization mechanisms for activity and selectivity, coupled with progress in design and synthesis of organometallic complexes.<sup>65,389</sup>

However, it is even more challenging for early transition metals to carry out the copolymerization of polar monomers, because the early metals are easily poisoned by the polar functional groups because they are inherently more oxophilic than late metals. In order to circumvent the poisoning by the polar groups, the functional group of the monomers is most often masked by protecting groups such as alkylaluminums or silyl groups.<sup>65,389</sup>

Hu and co-workers carried out the copolymerization of ethylene and 10-undecen-1-ol masked with  $^3Bu_3Al$  by using bis(phenoxy-imine) Zr or bis(phenoxy-ketimine) Zr or Ti complexes 132 or 192.<sup>191,496</sup> Complex 132 incorporated up to 8.15 wt % (1.48 mol %) 10-undecen-1-ol at the rate of 13 kg-polymer/(mmol-M·h), which was superior to the case of bis(phenoxy-imine) Zr complex 62 in terms of both comonomer uptake and activity. A typical metallocene, *rac*-( $C_2H_4$ )(1-indenyl) $ZrCl_2$ , yielded only a trace of polymer under the same conditions. A comparison between bis(phenoxy-ketimine) Zr and Ti complexes revealed that the Ti complex 192 showed higher tolerance to functional monomers than the corresponding Zr congener and gave copolymers having higher molecular weights and higher comonomer contents, although the Zr complex exhibited higher activity under the same conditions. It was also revealed that the comonomer uptake was large in the order 10-undecen-1-ol (1.10 mol %) > 10-undecenoic acid (0.56 mol %) > 5-hexen-1-ol (0.25 mol %) at the highest loading of the comonomer (1.2 mmol/L), irrespective of the metal center.

Table 25. Results of Ethylene/HA Copolymerization with the Phenoxy—Imine Ti Complexes<sup>a</sup>

complex	comonomer (mmol)	activity [g-polymer/ (mmol·M·h)]	comonomer content <sup>b</sup> (mol %)	$M_w^c$ (kg/mol)	$M_w^c/M_n^c$
88	1.00	86	0.13	497	2.1
90	1.00	337	0.81	269	2.2
193	1.00	341	0.90	273	2.2
194	1.00	515	0.74	387	2.4
195	1.00	353	0.66	252	2.2
196	1.00	178	0.50	190	2.4
197	1.00	28	d	d	d
90	2.00	68	1.97	59	1.8
193	2.00	71	1.90	69	1.7
194	2.00	61	1.82	67	2.2
195	2.00	56	1.98	55	1.8
196	2.00	17	d	d	d
90	5.25	11	2.45	20	1.8
193	5.25	15	3.20	23	1.6

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 20  $\mu$ mol; DMAO, 5.00 mmol; ethylene, 0.1 MPa; 25 °C; 10 min. <sup>b</sup> Determined by <sup>1</sup>H NMR.

<sup>c</sup> Determined by GPC (polystyrene calibration). <sup>d</sup> Not reported.

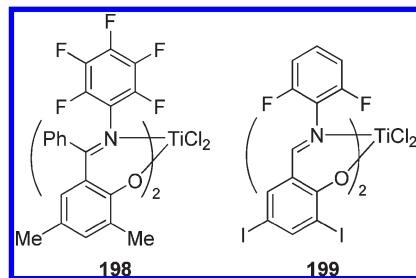
Fujita and co-workers took a further step toward the challenge not by masking the problem but by tuning catalyst properties in a rational manner. Copolymerization of ethylene with 5-hexen-1-yl acetate (HA) was examined with bis(phenoxy-imine) complexes activated with MAO.<sup>167</sup> Under the conditions at 4.0 mmol/L of HA, where the metallocene compounds  $Cp_2MCl_2$  (M: Ti, Zr) and CGC were completely inactive, all the bis(phenoxy-imine) group 4 metal complexes 88, 90, and 193–197 demonstrated the appreciable activities and comonomer uptake (Table 25). The bis(phenoxy-imine) Ti complexes showed higher activities and higher comonomer uptake than the Zr congener. Likewise, the phenyl group as  $R^2$  established higher activities and higher comonomer uptake than the  $R^2 = t$ -Bu group, as discussed in section 4.1.3.1.<sup>83</sup> Significantly, complexes 90 and 193 were still active at  $[HA] = 21.0$  mmol/L, which is higher than the concentration of MAO (20.0 mmol/L), indicating remarkable tolerance of the bis(phenoxy-imine) Ti complexes to the polar groups. The improved performance in both activity and comonomer uptake for the  $R^2 = Ph$  derivatives implies that the observed tolerance to the polar function is not caused simply by steric protection of the active metal centers by  $R^2$  (in this case, comonomer uptake is supposed to be inversely proportional to activity), but something electronic in nature must be involved. In fact, the calculations on the ethylene-coordinated and the carbonyl-coordinated species indicated that the energy differences between these two species ( $\Delta E$ ) for the bis(phenoxy-imine) Ti complexes were much smaller (37–61 kJ/mol) than those of the

metallocenes and CGC (>100 kJ/mol). Furthermore, by varying the electronic nature of the  $R^1$  substituents, it was revealed that electron withdrawing groups significantly decreased the copolymerization activities (complexes 196 and 197), which is opposite to the case of the ethylene homopolymerization, probably because of stronger coordination of the carbonyl group to the more electrophilic species. These results suggested that the nature of metals can be electronically tuned by ligands to tolerate the functional groups to a significant extent even with early metals.

**4.1.3.4. Block Copolymers.** The robust and versatile living polymerization catalysts based on bis(phenoxy-imine) Ti complexes have enabled the synthesis of a wide array of olefin block copolymers, which first appeared in the patent application of Mitsui Chemicals, Inc. in January 2000,<sup>450</sup> where diblock or triblock copolymers such as PE-*b*-sPP, PE-*b*-EPR, PE-*b*-EPR-*b*-sPP, PE-*b*-EPR<sup>1</sup>-*b*-EPR<sup>2</sup>, PE-*b*-EBR (EBR: poly(ethylene-*co*-but-1-ene)), sPP-*b*-EPR, sPP-*b*-EPR-*b*-PE, and EPR<sup>1</sup>-*b*-EPR<sup>2</sup>-*b*-PE were prepared (EPR<sup>1</sup> and EPR<sup>2</sup> stand for EPR having different compositions) by sequentially adding different monomers or monomer mixtures of different compositions. It is also to be noted that block copolymer synthesis can be started either by ethylene polymerization or propylene polymerization or their copolymerization, significantly widening the scope of attainable block structures.

Table 26 summarizes the olefin block copolymers, which have been prepared by means of living polymerization catalyzed by bis(phenoxy-imine) Ti catalysts. The thermal, morphological, mechanical, and optical properties of the block copolymers

**Table 26.** Olefin Block Copolymers Synthesized with the Living Polymerization Method Catalyzed by the Phenoxy–Imine or Phenoxy–Ketimine Ti Complexes



polymer	complex	$M_w/M_n$	$M_n$ (g/mol)	ref
PE- <i>b</i> -EPR	56	1.16	211,000	158
PE- <i>b</i> -EPR- <i>b</i> -sPP		1.15	235,000	
sPP- <i>b</i> -EPR	56	1.51	161,000	426
PE- <i>b</i> -PP	56	1.15	136,000	160
PE- <i>b</i> -EPR- <i>b</i> -PE		1.14	272,000	
sPP- <i>b</i> -EPR	152	1.12	145,100	79, 454
PE- <i>b</i> -poly(ethylene- <i>co</i> -cyclopentene)	152	1.32	211,000	490
PE- <i>b</i> -poly(ethylene- <i>co</i> -cyclopentene)- <i>b</i> -poly(ethylene- <i>co</i> -cyclopentene)		1.20	138,000	
PE- <i>b</i> -EPR	56	1.12	38,100	491
PE- <i>b</i> -polyhexene	88	n.r. <sup>a</sup>	n.r. <sup>a</sup>	446
sPP- <i>b</i> -EPR	152	1.09–1.12	47,000–106,600	492
EPR- <i>b</i> -iPP	198	1.10	90,000	90
PE- <i>b</i> -EHR	155	1.21–1.31	79,800–121,000	407
PP- <i>b</i> -EPR	152	1.14–1.31	73,600–570,000	493
poly(MCP- <i>co</i> -VTM)- <i>b</i> -poly(ethylene- <i>co</i> -NBE) <sup>b</sup>	152	1.41	451,000	494
EPR- <i>b</i> -poly(ethylene- <i>co</i> -NBE)		1.13	576,000	
PE- <i>b</i> -EPR	199	1.60	2,000,000	165
PE- <i>b</i> -EPR	199	1.4–2.0	550,000–2,000,000	495
PP- <i>b</i> -EPR				
PE- <i>b</i> -PS	199	1.5–1.8	390,000–900,000	487
EPR- <i>b</i> -PS		1.5–1.8	700,000–1,200,000	
iPP- <i>b</i> -EPR- <i>b</i> -iPP	169	1.13–1.30	102,000–235,000	91
iPP- <i>b</i> -EPR- <i>b</i> -EPR- <i>b</i> -iPP		1.15	195,000	
iPP- <i>b</i> -EPR- <i>b</i> -EPR- <i>b</i> -iPP- <i>b</i> -EPR- <i>b</i> -iPP		1.13	227,000	

<sup>a</sup> Not reported. <sup>b</sup> MCP, 1,3-methylenecyclopentane; VTM, 3-vinyldimethylethylene.

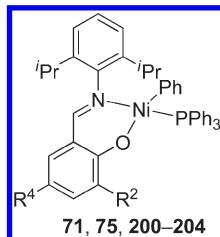
were examined in some instances, and these are discussed in section 10.4.

#### 4.2. Ni Complexes

In the category of phenoxy–imine-based olefin polymerization catalysts, nickel complexes have been the second most intensively investigated subject after group 4 metal complexes, as a direct result of a publication by the DuPont<sup>20</sup> and Grubbs groups in 1997.<sup>21</sup> As mentioned in section 3.2.2, a class of mono-(phenoxy–imine) Ni complexes of the type  $(L^{FI})NiR(L)$  have been prepared and examined for the polymerizations of ethylene,  $\alpha$ -olefins, styrene, cyclic olefins, and polar functional monomers and the copolymerization of these monomers. These complexes are active upon dissociation of the neutral donor ( $L$ ) under appropriate conditions, which allows an olefin monomer to coordinate and insert into the Ni–R bond. Bis-ligated complexes,  $(L^{FI})_2Ni$ , are naturally inactive to polymerization under these normal conditions, because no sites are available for the olefin insertion reaction.<sup>87,192,264</sup> Nevertheless, these complexes

can be active when activated with cocatalysts such as MAO or alkylaluminums in the presence of olefins, where they are assumed to be transformed into a monoligated complex of the type  $(L^{FI})NiR(\text{olefin})$ . In this section, ethylene polymerization by monoligated complexes and subsequently bis-ligated complexes will be discussed, followed by (co)polymerization of miscellaneous monomers using these complexes.

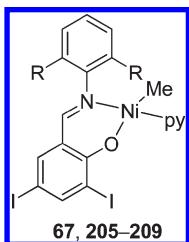
**4.2.1. Ethylene Polymerization.** When  $R^1 = 2,6-i\text{Pr}_2C_6H_3$  (complexes 71, 75, 200, 201, and 202), the ethylene polymerization activities increased with the size of the  $R^2$  substituents in the order 9-anthracyl > 9-phenanthrenyl > Ph >  $i\text{Bu}$  > H, which was also accompanied by increased polymer molecular weights and decreased branch contents (Table 27).<sup>22,264</sup> The branch contents were much lower than those which were obtained by the cationic Ni or Pd diimine complexes<sup>16</sup> under similar conditions, indicating that so-called chain walking (a chain end isomerization involving repetitive  $\beta$ -H elimination and rotation/reinsertion of the eliminated olefin)<sup>16</sup> was less frequent. It was considered that such a large  $R^2$  can enhance dissociation of

Table 27. Ethylene Polymerization Results for the Phenoxy–Imine Ni Complexes<sup>a</sup>

complex	R <sup>2</sup>	R <sup>4</sup>	activity [g-polymer/(mmol·M·h)]	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	branches/1000C
200	H	H	40	4.0	1.5	45
201	tBu	H	70	11.4	1.8	55
75	Ph	H	122	23.5	2.3	40
202 <sup>c</sup>	9-phenanthrenyl	H	373	37.7	3.8	30
71 <sup>c</sup>	9-anthracyl	H	395	54.0	3.8	30
203	H	OMe	20	7.3	1.7	53
204 <sup>d</sup>	H	NO <sub>2</sub>	380	360	12.4	22

<sup>a</sup> Polymerization conditions: toluene, 90 mL; complex, 75 μmol; Ni(cod)<sub>2</sub>, 150 μmol; ethylene pressure, 0.69 MPa; no temperature control, 40 min.

<sup>b</sup> Determined by GPC (polyethylene calibration). <sup>c</sup> 15 min. <sup>d</sup> More solvent added during the reaction.

Table 28. Effects of the R<sup>1</sup> of the Phenoxy–Imine Ni Complexes on the Ethylene Polymerization Behavior<sup>a</sup>

complex	R	activity [kg-polymer/(mmol·M·h)]	M <sub>n</sub> <sup>b</sup> (kg/mol)	branches/1000C <sup>c</sup>
205	Ph	0.45	2.9	52
67	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1.17	19	10
206	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	0.15	11	26
207	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1.20	1.1	76
208	3,5-(OMe) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1.25	1.9	79
209	tPr	0.21	12	5

<sup>a</sup> Polymerization conditions: toluene, 100 mL; ethylene, 4 MPa; complex, 40 μmol; 50 °C; 0.5 h. <sup>b</sup> Determined by GPC (polyethylene calibration). <sup>c</sup> Predominantly methyl branches.

the phosphine ligand and also prevent a deactivation caused by formation of bis-ligated complexes through disproportionation, thereby accelerating olefin insertion and extending catalyst life. This was verified by the fact that the activity was indeed enhanced by using the complexes that have a more labile neutral donor instead of Ph<sub>3</sub>P.<sup>69,87,298,299</sup> The bulky R<sup>2</sup> may sterically retard chain migration and chain transfer, in accord with the increased molecular weights and the decreased branch numbers.

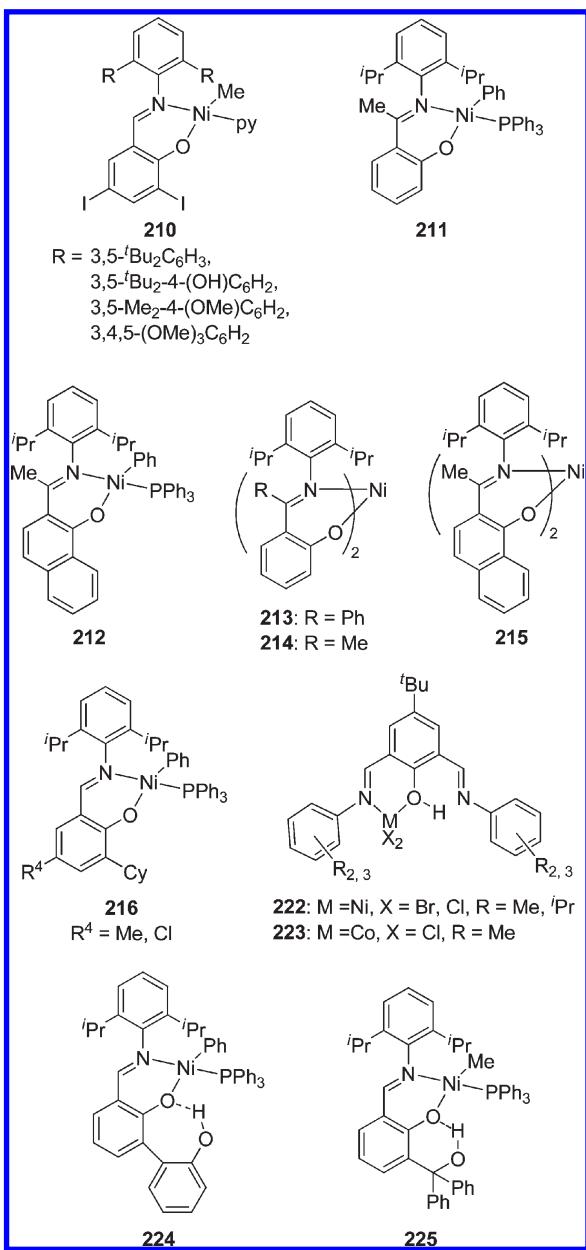
When R<sup>2</sup> = H, the electronic perturbations of R<sup>4</sup> were investigated, albeit with limited scope.<sup>22</sup> The highest polymerization activity was observed for R<sup>4</sup> = NO<sub>2</sub> (204: 380 g-polymer/(mmol·M·h)), followed by some modest ones for H (200: 40 g-polymer/(mmol·M·h)) and OMe (203: 20 g-polymer/

(mmol·M·h)). The molecular weight obtained by NO<sub>2</sub>-complex 204 was much higher (M<sub>w</sub> 360 kg/mol, polystyrene calibration) than the others (4.0, 7.3 kg/mol) despite the lack of bulky R<sup>2</sup> substituents, and also the PDI value of the PE was very large (12.4) for an unknown reason. In fact, a computational study on the nitro complex was not in accord with the experimental results, suggesting that the nitro group was significantly deviated from an electronically linear relationship.<sup>381</sup> Complex 204 (R<sup>4</sup> = NO<sub>2</sub>) was also peculiar in that the polymerization started after a very long induction period (~20 min), probably because of slow dissociation of the phosphine donor due to the strengthened Ni–P bond by an electron withdrawing NO<sub>2</sub> group.

When R<sup>2</sup> = R<sup>4</sup> = iodine, 2,6-diaryl substituted phenyl groups as R<sup>1</sup> (complexes 67 and 205–208) were investigated by Mecking and co-workers and compared with the common 2,6-diisopropylphenyl group (complex 209).<sup>69</sup> In general, 2,6-diaryl substitution is beneficial to the activity enhancement relative to 2,6-diisopropyl groups. Interestingly, the substituents at the 3,5-positions on the 2,6-diaryl groups demonstrated a significant influence on the activity duration and the molecular weight and branch frequency of the obtained PEs (Table 28). Although the initial activities for those 2,6-diaryl substituted complexes seemed to be equally high, the lack of substituents at the 3,5-positions (complexes 205 and 206) caused rather rapid deactivation, presumably due to C–H bond activation or formation of bis-ligated complexes. General increase of molecular weight and decrease of branch contents caused by electron withdrawing groups at the 3,5-positions were supposed to be attributed to restraints of the chain transfer and chain walking reactions by the electron withdrawing groups.<sup>69</sup> Bulky 3,5-substituents such as tBu groups could achieve similar results on the molecular weights and microstructures of the polymers.<sup>296</sup> However, the influences of para-substitution of the 2,6-diaryl groups were revealed to be purely electronic, and the electron withdrawing groups enhanced the polymerization activities, the polymer molecular weights, and the linearity of the obtained PEs (less branching).<sup>297</sup>

9-Anthracyl and iodine as the R<sup>2</sup> substituent appeared to exert a similar influence on the polymerization characteristics

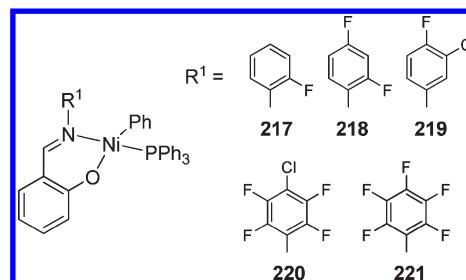
Chart 14



when combined with the terphenyl  $R^1$  groups. More specifically, the nature of the terphenyl  $R^1$  groups determined the branch contents irrespective of  $R^2$  or  $R^4$  (67, 207, 208, and 210), although the activities were significantly varied by the nature of  $R^2$  and  $R^4$ .<sup>296</sup>

Carlini and co-workers employed a mixture of phenoxy-imine ligands, ( $L^{FI}$ )—H, and  $\text{Ni}(\text{cod})_2$  for ethylene polymerization, where the oxidative addition of ( $L^{FI}$ )—H to the Ni-bound cyclooctadiene was assumed to generate a 5-cyclooctenyl Ni species with liberation of a cyclooctadiene molecule (35, Scheme 14).<sup>294</sup> Especially when the phenoxy group had  $\text{NO}_2$  group(s) as  $R^2$  and/or  $R^4$  substituents and therefore the phenolic OH groups were more acidic, the *in situ* generated species exhibited appreciable activities toward ethylene polymerization and gave high molecular weight polymers. The alkyl-olefin

**Table 29.** Ethylene Oligomerization Results for the Phenoxy–Imine Ni Complexes<sup>a</sup>

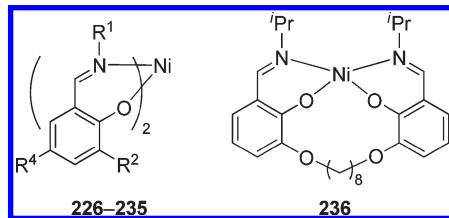


<sup>a</sup> Oligomerization conditions: toluene, 30 mL; complex, 1.5  $\mu\text{mol}$ ; ethylene pressure, 1.2 MPa; 25 °C; 0.5 h.

chelate species 35 themselves appeared to be inactive to ethylene polymerization. An appropriate amount of MAO was believed to transform it into a Ni–Me species. Since the information on the molecular weight distribution of the polymers was not given, it is not clear that these polymerizations take place via a single site mechanism. In many respects, these catalysts seemed to behave differently from the well-defined isolated complexes described above. This may be attributable to the peculiarity of  $\text{NO}_2$  groups as mentioned above.

Mono- and bis-ligated phenoxy–ketimine complexes 211–215 were synthesized by Abu-Surrah, Repo, and their co-workers (Chart 14). These phenoxy–ketimine ligands were found to be prone to form bis-complexes easily, and even monoligated complexes 211 and 212 were completely inactive for ethylene or NBE polymerizations.<sup>270</sup> Complexes 216, bearing a cyclohexyl  $R^2$  group, were prepared and examined by Sun and co-workers for ethylene homo- and copolymerization with polar monomers.<sup>81,82</sup> These complexes exhibited several hundred grams-polymer/(mmol-M·h) of activity upon activation with  $\text{Ni}(\text{cod})_2$  or alkylaluminums for both  $R^4$  substituents (Me or Cl), roughly comparable to those for the typical Grubbs complex. Other polymerization characteristics also appeared to be similar. The complexes having fluorinated  $N$ -aryl groups (217–221) were found to serve as an ethylene oligomerization catalyst (C<sub>4</sub> and C<sub>6</sub> olefins) with MAO, of which activities became higher with the number of substituted halogens (Table 29).<sup>272</sup> This seems to be consistent with the general relationship between steric bulk and the electronic nature of  $R^1$  and the  $\beta$ -H elimination and activity, as discussed above. Ni complexes having a ligand that had two Schiff bases at the 2- and 6-positions of a phenol moiety (complexes 222) were prepared.<sup>260,263</sup> The phenolic-OH was not deprotonated under the studied conditions, and therefore, these ligands served as a neutral ligand in these examples. These complexes induced ethylene oligomerization upon activation with MAO (10<sup>2</sup>–10<sup>3</sup> g-oligomers/(mmol-M·h·bar)).

Table 30. Ethylene Oligomerization Results for the Bis(phenoxy-imine) and Tetradeinate Phenoxy-Imine Ni Complexes



complex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	cocatalyst	C <sub>2</sub> H <sub>4</sub> pressure (MPa)	activity [kg-oligomer/(mmol-M·h·bar)]	ref
226 <sup>a</sup>	<sup>i</sup> Pr	H	H	MAO	2	0.154	80
227 <sup>a</sup>	<sup>t</sup> Bu	H	OMe	MAO	5	0.258	80
228 <sup>a</sup>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	<sup>i</sup> Bu <sub>3</sub> Al	6	0.00294	80
228 <sup>a</sup>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	MAO	5	5.26	80
229 <sup>a</sup>	2,6- <sup>i</sup> Pr <sub>2</sub> -cyclohexyl	H	H	MAO	5	1.34	80
236 <sup>a</sup>				MAO	5	~0	80
230 <sup>b</sup>	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	516 <sup>d</sup>	314
231 <sup>b</sup>	2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	544 <sup>d</sup>	314
228 <sup>b</sup>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	518 <sup>d</sup>	314
232 <sup>b</sup>	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<sup>t</sup> Bu	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	573 <sup>d</sup>	314
233 <sup>b</sup>	2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<sup>t</sup> Bu	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	529 <sup>d</sup>	314
234 <sup>b</sup>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<sup>t</sup> Bu	H	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	0.13	621 <sup>d</sup>	314
235 <sup>c</sup>	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CHO	Cl	MAO	0.1	0.0768	312

<sup>a</sup> Oligomerization conditions: toluene, 10 mL; complex, 5–50 μmol; Al/Ni = 10–1000; 25 °C; 1 h. <sup>b</sup> Oligomerization conditions: toluene, 80 mL; complex, 13.6 μmol; Al/Ni = 200; 30 °C; 1 h. <sup>c</sup> Oligomerization conditions: toluene, 35 mL; Al/Ni = 1000; 15 °C; 20 min. <sup>d</sup> See ref 497.

The cobalt analogues **223** afforded C<sub>4</sub>–C<sub>6</sub> olefins, albeit at very low efficiency (see section 4.3.4).

Li and co-workers synthesized a complex that had an intramolecular hydrogen bond with the phenolic oxygen and tested it in ethylene polymerizations.<sup>273</sup> Complex **224** showed up to 1.14 kg-polymer/(mmol-M·h) of activity (40 °C, 2.1 MPa ethylene pressure), somewhat higher than that of a similar phenyl complex,<sup>264</sup> although direct comparison was not made. For the possible activity enhancement, involvement of the hydrogen bond was suggested. This concept was established by a similar complex **225** prepared by Marks and co-workers recently.<sup>288</sup> The complex that possessed an intramolecular hydrogen bond achieved considerably higher activities than the analogous complexes without such intramolecular hydrogen bonds. Since the intramolecular hydrogen bond is considered to reduce the electron density of the phenolic oxygen and, thus, that at the metal center, the enhanced activity observed for this complex is in line with the general characteristics for electron withdrawing groups discussed in section 3.3. The complex also exhibited higher branch contents, smaller polymer molecular weights, and, interestingly, higher tolerance to polar additives. It was proposed that the hydroxyl group involved in the intramolecular hydrogen bond would work as a local scavenger to the polar additives.

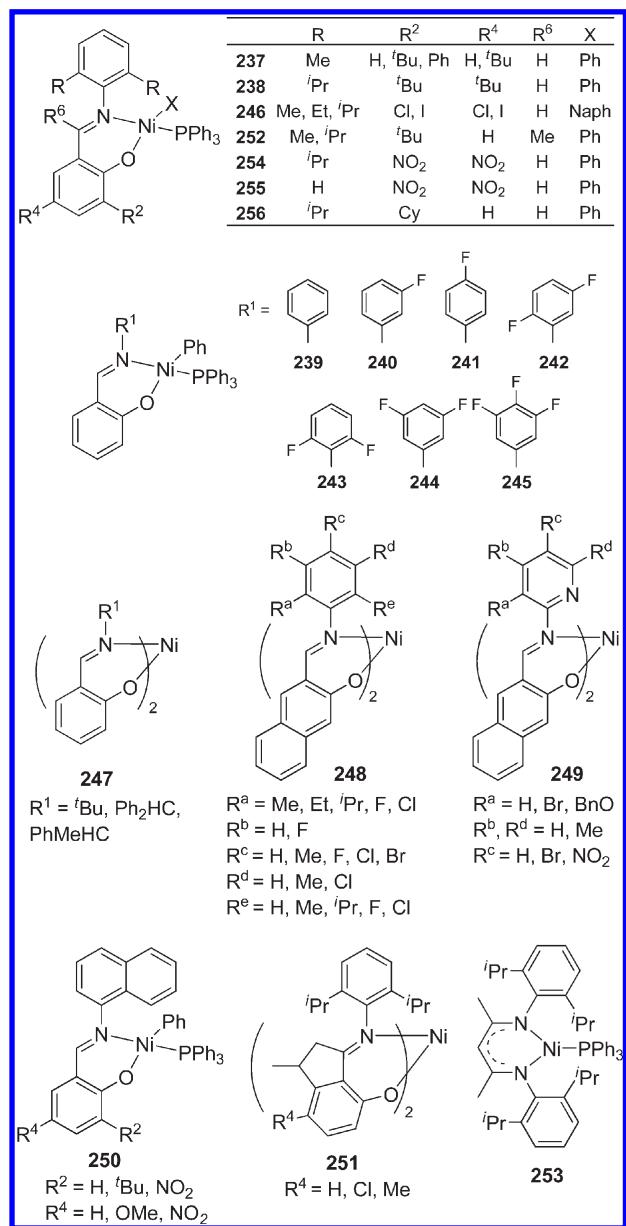
Grubbs and co-workers briefly reported that even a bis-ligated complex gave a small amount of PE when activated with MAO.<sup>264</sup> A number of bis-ligated Ni complexes (**226–236**) (Table 30) were revealed by several groups to be extremely active ethylene oligomerization catalysts (up to 620 kg-oligomers/(mmol-M·h·bar))<sup>497</sup> upon activation with alkylaluminums (R<sub>3</sub>Al, MAO, Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>), affording mostly C<sub>4</sub> and C<sub>6</sub> olefins.<sup>80,312,314</sup> The formation of a monoligated alkyl complex was assumed at relatively low Al/Ni ratios (~100) using UV-vis spectroscopy.<sup>80,314</sup>

A clear trend was not observed for the influences of the alkyl or alkoxy substituents examined in these works. However, Carlini and co-workers revealed that introduction of nitro groups as R<sup>2</sup> and R<sup>4</sup> substituents dramatically altered the characteristics of the complexes into ethylene polymerization catalysts.<sup>383</sup> The peculiarity of the nitro groups appeared to override the influences of the other substituents; that is, the obtained polymers were high in molecular weight ( $M_v = 10^5$  g/mol) and low in branch density, independent of R<sup>1</sup> (C<sub>6</sub>H<sub>5</sub> or 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Under the optimized conditions, the complex achieved 1.9 kg-polymer/(mmol-M·h) at 5 MPa of activity, although the PDI value was significantly large (13–15).<sup>385</sup> Gibson and co-workers prepared bis(phenoxy-imine) Ni complexes that had a ferrocenyl group as R<sup>1</sup>, although they were inactive to ethylene oligomerization or polymerization.<sup>192</sup> A tetradeinate Ni salphen complex can oligomerize ethylene into C<sub>4</sub>–C<sub>10</sub> olefins at high temperature (110–200 °C).<sup>498</sup>

**4.2.2. Polymerization of Other Monomers.** Ni or Pd complexes with appropriate cocatalysts are known to polymerize NBE into high molecular weight polymers in a “metal-mediated coordination insertion mechanism” with high activities.<sup>394,499,500</sup> Note: In the following examples where phenoxy-imine Ni complexes were applied for NBE polymerization, the polymerizations were carried out, as in other reports, in a batch reactor, to which NBE was added in one portion at the beginning. Care must be taken when activities (in kg-polymer/(mmol-M·h)) are discussed because the activity numbers given in the papers usually did not consider the concentration of NBE and its variance with reaction time. Therefore, cross-referential comparison of the activities should not be made in a strict sense for the values appearing in this section.

Borkar and Saxena reported that Ni salen complexes could polymerize NBE with MAO,<sup>501</sup> Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>,<sup>502</sup> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>503,504</sup>

Chart 15



Li et al. examined a wide variety of *N*-aryl mono(phenoxy-imine) Ni complexes 237, 238, 200, 201, and 75 bearing alkyl substituents on *N*-aryl and phenoxy moieties for NBE polymerization using modified MAO (MMAO) as a cocatalyst and obtained high molecular weight poly(NBE) ( $M_v > 10^6$  g/mol) in high yields but without substantial differences derived from the substituents.<sup>505</sup> The electronic effects of  $\text{R}^1$  were also investigated using the monoligated complexes bearing fluorinated *N*-aryl groups (complexes 217, 218, 221, and 239–245; Chart 15).<sup>274</sup> The activity enhancement by fluorination was evident but relatively minor in intensity.

Likewise, the complexes 246 bearing chlorine or iodine as  $\text{R}^2$  and  $\text{R}^4$  were examined by Sun and co-workers in conjunction with MAO.<sup>283</sup> A polymerization at high [NBE] in a short reaction period (20 s) exhibited an activity of 265 kg-polymer/(mmol-M·h) (NBE conversion 78%), although the PDI was

**Table 31. Ethylene Polymerization with the Phenoxy–Imine Ni Complex in the Presence of Functional Additives<sup>a</sup>**

complex	additive	activity [kg-polymer/(mmol-M·h)]	$M_w$ (kg/mol)	$M_w/M_n$
71	dimethoxyethane	0.49	270	2.4
71	diethyl ether	0.31	241	2.0
71	acetone	0.08	131	3.7
71	ethylacetate	0.07	188	2.0
71	water	0.05	90.1	2.0
71	ethanol	0.02	46.6	3.0
71	trimethylamine	0.01	28.2	2.6

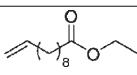
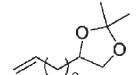
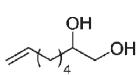
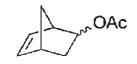
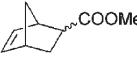
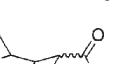
<sup>a</sup> Polymerization conditions: toluene, 90 mL; complex, 65  $\mu\text{mol}$ ; ethylene, 100 psig (0.69 MPa); additive, 10 mL (>1500 equiv); 10 °C; 3 h.

of the obtained polymers showed relatively large values ( $M_w/M_n = 3–9$ ). When  $\text{R}^1$  was varied in bis-ligated complexes 247 and 226, the activities followed the order  $\text{R}^1 = \text{Ph}_2\text{HC} > \text{PhMeHC} > \text{iPr} > \text{tBu}$ , implying that the steric bulk of  $\text{R}^1$  was apparently important. The importance of [NBE] was underlined again, and the activity of 423 kg-polymer/(mmol-M·h) was achieved at 5.0 M [NBE] in a 15 s polymerization (NBE conversion 47%).<sup>317</sup> A further diverse library on aryl  $\text{R}^1$  groups was investigated with 2-naphthoxy-based Ni bis-ligated complexes 248 and 249.<sup>318</sup> The complexes bearing 2-pyridyl derivatives as  $\text{R}^1$  afforded poly(NBE) with narrower PDI values of around 2 compared to those bearing aryl  $\text{R}^1$  groups.

Monoligated Ni complexes 250 having a 1-naphthyl group as  $\text{R}^1$  showed substantially higher activity than that of the  $\text{R}^1 = \text{phenyl group}$ , although the polymerization characteristics were rather insensitive to electronic or steric perturbations on the  $\text{R}^2$ ,  $\text{R}^4$  substituents.<sup>271</sup> Similarly, bis(phenoxy–ketimine) Ni complexes 251, where the alkyl group of the ketimine moiety was fused with the phenoxy ring (indanimine), were examined for NBE polymerization.<sup>331</sup> Upon activation with MAO, they exhibited appreciable activities, which were claimed to be higher than those of similar phenoxy–imine complexes. An interesting comparison was made between Ni complexes 252, 253, 370, and 371 (Table 38) bearing three different Schiff base ligands. These complexes were active and behaved as a single site catalyst in NBE polymerization activated by MMAO and were apparently similar to each other in polymerization characteristics.

Carlini and co-workers employed bis-ligated complexes having nitro  $\text{R}^2$  and  $\text{R}^4$  groups (254, 255, and 200). With  $\text{R}^1 = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ , nitro groups do not seem as effective as the authors claim (254:  $\text{R}^2 = \text{R}^4 = \text{NO}_2$ , 42 g-polymer/(mmol-M·h),  $M_w$  180 kg/mol; 200:  $\text{R}^2 = \text{R}^4 = \text{H}$ , 36 g-polymer/(mmol-M·h),  $M_w$  150 kg/mol).<sup>386</sup> Also, with  $\text{R}^2 = \text{R}^4 = \text{NO}_2$ ,  $\text{R}^1$  variants ( $2,6\text{-iPr}_2\text{C}_6\text{H}_3$  or  $\text{C}_6\text{H}_5$ ) did not show any marked differences (255:  $\text{R}^1 = \text{C}_6\text{H}_5$ , 42 g-polymer/(mmol-M·h),  $M_w$  196 kg/mol). Under appropriate conditions using chlorobenzene as solvent, the activity of complex 254 reached 35 kg-polymer/(mmol-M·h). Chen, He, and their co-workers carried out copolymerization of NBE and 5-norborn-2-yl-acetate using a bis( $\beta$ -ketimine)Ni complex/ $\text{B}(\text{C}_6\text{F}_5)_3/\text{Et}_3\text{Al}$ .<sup>506</sup>

As discussed in section 3.4, vinyl-functionalized monomers such as methyl acrylate (MA) cause irreversible deactivation of the active species derived from mono(phenoxy–imine) Ni complexes via a relatively stable chelated Ni species, which is formed upon 2,1-insertion of MA.

complex	comonomer	comonomer (M)	[comonomer]/[Ni]	ethylene (psig)	ethylene TON <sup>b</sup>	comonomer TON <sup>b</sup>	branches/1000C <sup>c</sup>	$M_w$ (kg/mol)	$M_w/M_n$	comonomer incorporation <sup>d</sup> (mol%)
65		0.72		100	12,400	25	8	165	2.5	0.2
65		0.72		100	6080	19	5	172	2.3	0.2
65		0.72		100	1362	5	8	54	2.4	0.3
71			0.16	100	458	34	9	17	1.6	5
71			0.14	100	1540	39	9	70	2.1	4
65			0.36	100	2474	60	9	74	1.6	2
65			0.14	<5	102	51	— <sup>e</sup>	30	1.2	31
65			0.36	100	8585	200	14	41	1.6	4
65			0.18	100	1360	5	5	59	2.9	0.3
65'		0.02		20	3240	20	43	— <sup>g</sup>	— <sup>g</sup>	0.5
65		0.13	100	7600	8	7	— <sup>g</sup>	— <sup>g</sup>	— <sup>g</sup>	0.1

<sup>a</sup>Polymerization conditions: toluene, 90 mL; complex, 65 μmol (0.72 mM); 40 °C; 8 h. <sup>b</sup>TON = mol of substrate converted/mol of catalyst.

<sup>c</sup>Total Me + Et + Pr + Bu branches per 1000 carbons. <sup>d</sup>Determined by <sup>13</sup>C NMR. <sup>e</sup>No branches observed. <sup>f</sup>2,6-Di-*tert*-butylpyridine was added to the monomer solution before the reaction. <sup>g</sup>Data not reported.

Figure 9. Copolymerization of ethylene with functionalized monomers with the phenoxy-imine Ni complex.<sup>a</sup>

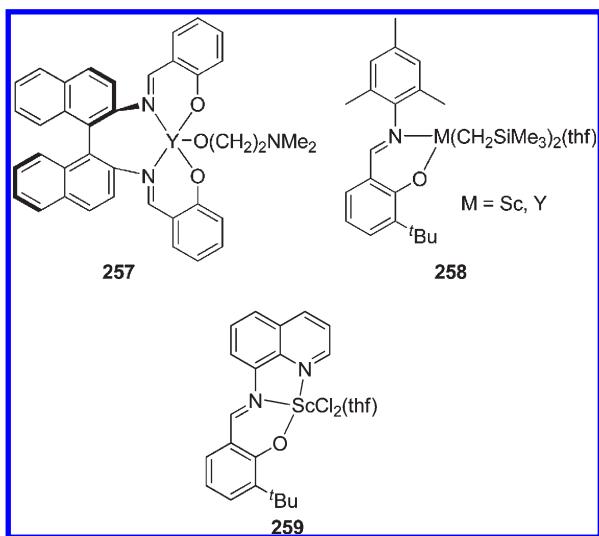
Nevertheless, homopolymerization of methyl methacrylate was reported by Carlini and co-workers using bis-ligated Ni complexes<sup>305,313</sup> or in situ generated species from ( $L^{FI}$ )–H/Ni( $cod$ )<sub>2</sub>.<sup>295</sup> A metal-mediated polymerization mechanism was suggested for these polymerizations based on the experiment in the presence of a radical inhibitor. However, considering that a phenol-based radical trap was often not effective for inhibiting free radical chain propagation particularly in the presence of MAO,<sup>388,389</sup> coupled with syndio-rich tacticity and very large PDI values of the obtained polymers, possible involvement of radical processes cannot be excluded. Similar caution is also necessary regarding radically polymerizable (cationic or anionic path is also possible) styrene polymerization using the same systems.<sup>307</sup> Jin and co-workers also employed bis(phenoxy-indanimine) Ni complexes for polymerization of MMA<sup>330</sup> and styrene<sup>307</sup> using MAO as a cocatalyst.

4.2.3. Copolymerization of Ethylene and Polar Functional Comonomers. Even though homopolymerization of vinyl-

functionalized polar monomers seems to be difficult even with the neutral phenoxy-imine Ni complexes, they showed remarkable tolerance to the functional groups, which has been exemplified in three ways: (1) polymerization in the presence of polar additives; (2) copolymerization with certain polar monomers; and (3) emulsion polymerization in biphasic media (see sections 9.3 and 10.2 for emulsion polymerization).

Grubbs and co-workers demonstrated that when a variety of polar additives such as ether, ketone, ester, water, alcohol, and tertiary amine were added in large excess (~1500 equiv to Ni), complex 71 can still polymerize ethylene at significant rates (Table 31).<sup>264</sup> It was also shown that polar functional olefins having adequate spacers between functional groups and olefinic groups were actually enchainable in ethylene copolymerizations by complexes 71 and 65 without the aid of masking by Lewis acidic additives such as alkylaluminums (Figure 9).<sup>264,265</sup> Bicyclic olefins were more reactive and more readily incorporated into PEs than  $\alpha$ -olefins, presumably due to their ring-strain and

Chart 16



release of it upon insertion. Interestingly, less-branched polymers were formed in the presence of polar monomers or additives. Sun and co-workers employed complexes **256** bearing a cyclohexyl  $\text{R}^2$  group for ethylene (co)polymerization in the presence of polar substances and polar comonomers, which demonstrated similar polymerization characteristics.<sup>81,82</sup> They employed  $\text{Bu}_3\text{Al}$  as a phosphine scavenger, which showed somewhat lower activities than those with  $\text{Ni}(\text{cod})_2$ .

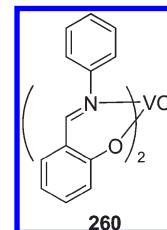
As already discussed (section 4.2.2),  $(\text{L}^{\text{FI}})_2\text{Ni}/\text{MAO}$  or  $(\text{L}^{\text{FI}})-\text{H}/\text{Ni}(\text{cod})_2/\text{MAO}$  catalyst systems developed by Carlini and co-workers exhibited polymerization activities toward ethylene and MMA, although the active species including the possible involvement of radical species were not explicitly demonstrated. These catalysts gave a mixture of polymers that could be fractionated by solvents. Again, the obtained polymers possessed extremely large PDI values (30–60) even after fractionation (10–25).<sup>306</sup> The apparent contents of MMA in the products were 60–80 mol % for  $(\text{L}^{\text{FI}})_2\text{Ni}/\text{MAO}$  and 3–6 mol % for nitro group containing  $(\text{L}^{\text{FI}})-\text{H}/\text{Ni}(\text{cod})_2/\text{MAO}$ .

#### 4.3. Phenoxy–Imine Complexes with Other Metals

**4.3.1. Scandium and Yttrium Complexes.** Scandium and yttrium metallocene complexes ( $\text{Cp}'_2\text{M}-\text{R}$ ; M: Sc, Y) have been extensively examined as an isoelectronic species of a 14e cationic  $[\text{Cp}'_2\text{M}-\text{R}]^+$  species derived from group 4 metallocenes.<sup>508,509</sup> In recent years, it was demonstrated that more electron deficient species,  $[\text{Cp}'\text{M}-\text{R}]^+$ , exhibited a number of interesting polymerization characteristics toward ethylene, styrene, cyclic olefins, and conjugated dienes.<sup>509</sup> Within this context, the chemistry of group 3 elements was applied also to other ancillary ligands including phenoxy–imine ligand systems, and several examples of  $(\text{L}^{\text{FI}})_2\text{MR}$  or  $(\text{L}^{\text{FI}})\text{MR}_2$  (**23**, **257**, **258**, and **259**; Chart 16) were reported by Coates,<sup>510</sup> Bochmann,<sup>138</sup> Piers,<sup>139</sup> Paolucci, and Longo.<sup>140</sup> While these complexes were effective catalysts for lactide or  $\epsilon$ -caprolactone polymerization,<sup>138,510</sup> the activities for ethylene polymerization were rather sluggish, insofar as reported.<sup>139,140</sup>

**4.3.2. Group 5 Metal Complexes.** Vanadium complexes such as  $\text{V}(\text{acac})_3$  (acac: acetylacetone) or  $\text{VOCl}_3$  combined with alkylaluminum halides have been known to serve as a soluble

Table 32. Ethylene Polymerization with the Phenoxy–Imine V Complex and  $\text{VOCl}_3$ <sup>a</sup>



complex	$T_p$ <sup>b</sup> (°C)	$\text{MgCl}_2$	$\text{Et}_3\text{Al}$	activity [kg-polymer/(mmol·M·h)]
<b>260</b>	25	0	0	20.0
<b>260</b>	75	0	0	4.90
<b>260</b>	25	0.80	2.40	18.7
<b>260</b>	75	0.80	2.40	65.1
$\text{VOCl}_3$	25	0	0	12.6
$\text{VOCl}_3$	75	0	0	5.60
$\text{VOCl}_3$	25	0.80	2.40	8.30
$\text{VOCl}_3$	75	0.80	2.40	5.40

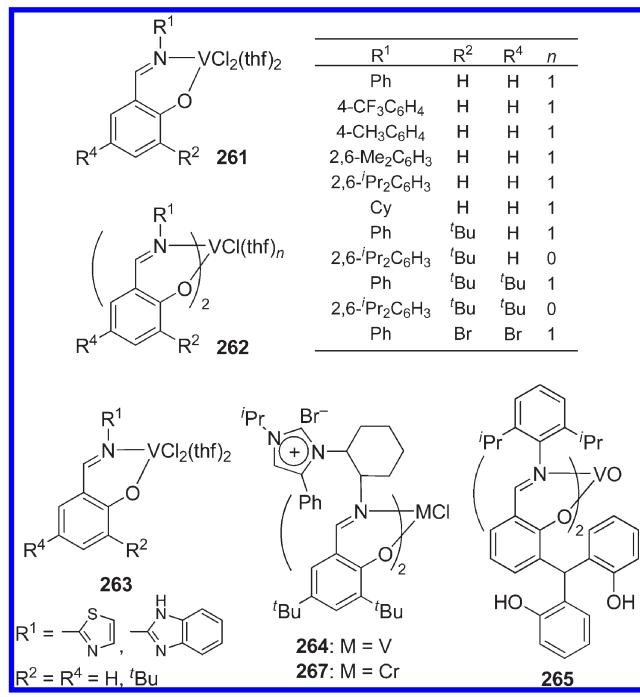
<sup>a</sup> Polymerization conditions: toluene, 400 mL;  $\text{Et}_2\text{AlCl}$ , 0.4 mmol; ETA, 0.4 mmol; complex, 1.0  $\mu\text{mol}$ ; 15 min. <sup>b</sup> Polymerization temperature.

single site catalyst since the early stages of Ziegler–Natta catalyst development, and they are today being used in the making of EPR and ethylene/propylene/diene elastomers (EPDM).<sup>511,512</sup> These V catalysts perform better with alkylaluminum halides rather than trialkylaluminums or MAO as a cocatalyst, and they are thought to be active in their high oxidation states (V(III) to V(V)) and to be deactivated by being reduced to V(II). In order to suppress the reduction, the polymerizations are usually carried out at relatively low temperature and often with a mild oxidizing agent such as butylperchlorocrotonate (BPCC:  $\text{CCl}_3\text{CCl}=\text{CCCOOC}_2\text{H}_9$ ) or ethyltrichloroacetate (ETA:  $\text{CCl}_3\text{COOC}_2\text{H}_5$ ) as an activator.

Floriani and co-workers prepared a variety of vanadium(III) and vanadium(IV) complexes bearing phenoxy–imine ligands and established their coordination chemistry.<sup>37,237,238,513,514</sup> Milani and co-workers employed a wide variety of Schiff base vanadium complexes,  $(\text{L}^{\text{FI}})_2\text{VO}$  and  $(\text{L}^{\text{FI}})_3\text{V}$  for ethylene/propylene copolymerizations (cocatalyst and activator were  $\text{Et}_2\text{AlCl}$  and BPCC or ETA, respectively), concluding that no clear structure–activity/selectivity relationships were observed.<sup>35</sup>

A solution to the drawback of the thermal instability of the vanadium catalysts was provided by Fujita and co-workers. They found that the  $\text{MgCl}_2$ -based compounds,  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , which can be prepared by dealcoholysis of  $\text{MgCl}_2/\text{ROH}$  (R: 2-ethylhexyl) adducts by  $\text{Et}_3\text{Al}$ , worked as an excellent cocatalyst as well as a solid support specifically for metal complexes bearing heteroatom containing ligands (see section 9.2). In this framework, addition of the  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  to the  $(\text{L}^{\text{FI}})_2\text{VO}$  (**260**)/ $\text{Et}_2\text{AlCl}/\text{ETA}$  catalyst system resulted in a marked improvement in the thermal stability of the catalyst, which showed an activity of 65.1 kg-polymer/(mmol·M·h) at 75 °C (vs 20 kg-polymer/(mmol·M·h) without the  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ ) (Table 32).<sup>26,515–517</sup> The observed very high activity at 75 °C lasted at least 1 h (vs <15 min for  $\text{VOCl}_3$ ) under the given conditions and afforded extremely high molecular weight PEs that had well regulated morphology, meaning that the

Chart 17



$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  was indeed serving as a catalyst support. This surprising activity improvement was not observed at 25 °C or with  $\text{VOCl}_3$  instead of the phenoxy-imine complex, indicating contributions from both the phenoxy-imine ligand and the  $\text{MgCl}_2$  support for realizing the unusually thermally robust V based catalysts.

Li and co-workers investigated mono- and bis(phenoxy-imine) V complexes,  $(\text{L}^{\text{FI}})\text{VCl}_2(\text{thf})_2$  (261; Chart 17), and  $(\text{L}^{\text{FI}})_2\text{VCl}(\text{thf})_n$  ( $n: 0, 1$ ) (262) for their ethylene polymerization behavior.<sup>240</sup> Most of these complexes demonstrated activities of 10–20 kg-polymer/(mmol-M·h·bar) and afforded linear PEs of  $M_w = 3–17 \times 10^4$  g/mol, when activated with  $\text{Et}_2\text{AlCl}/\text{ETA}$ . For a series of  $(\text{L}^{\text{FI}})\text{VCl}_2(\text{thf})_2$  (261), it was revealed that  $\text{R}^2$  substituents (<sup>t</sup>Bu or Br) decreased polymerization activities relative to  $\text{R}^2 = \text{H}$ , although the bulky  $\text{R}^1$  (2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R: Me, iPr) did not harm the activities relative to  $\text{R}^1 = \text{Ph}$ . The electronic perturbations on  $\text{R}^1$ , either electron withdrawing or donating, deteriorated the activities (4-XC<sub>6</sub>H<sub>4</sub>; X: CF<sub>3</sub>, Me). The bis-ligated complexes,  $(\text{L}^{\text{FI}})_2\text{VCl}(\text{thf})_n$  (262), exhibited roughly comparable activities to monoligated complexes, although the polymerization characteristics were seemingly different. The bulky  $\text{R}^2$  substituents (<sup>t</sup>Bu or Br) combined with  $\text{R}^1 = \text{Ph}$  resulted in nearly equivalent or better activities relative to  $\text{R}^2 = \text{H}$ , but with  $\text{R}^1 = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ , the activities of the complexes bearing  $\text{R}^2 = \text{H}$  became extremely low relative to the other complexes. The electronic effects on  $\text{R}^1$  appeared to be at work, since the activities increased in the following order:  $\text{R}^1 = 4\text{-}(\text{CF}_3)\text{C}_6\text{H}_4 > \text{C}_6\text{H}_5 > 4\text{-}(\text{OMe})\text{C}_6\text{H}_4$ . By using a monoligated complex 261 ( $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{R}^4 = \text{H}$ ), copolymerization of ethylene with 10-undecen-1-ol masked with 1 equiv of  $\text{Et}_2\text{AlCl}$  afforded a copolymer of 4.0 mol % comonomer content at an activity of 8.70 kg-polymer/(mmol-M·h·bar).<sup>518</sup> Heterocyclic aromatic groups were employed as  $\text{R}^1$  (complexes 263), which showed enhanced thermal stability in ethylene (co)polymerizations.

Scheme 28

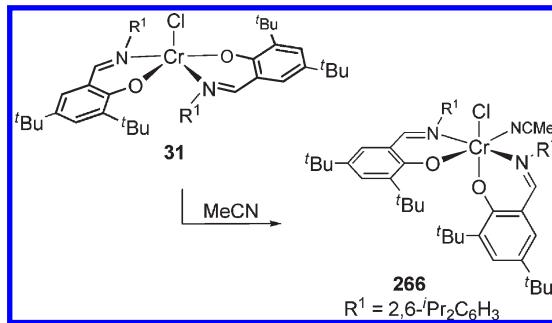
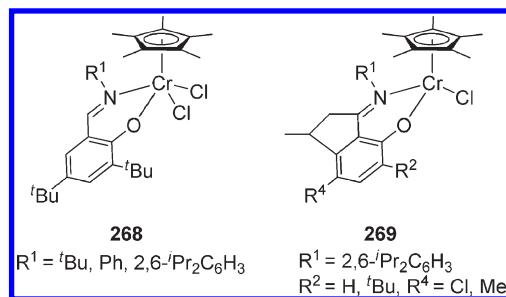


Chart 18



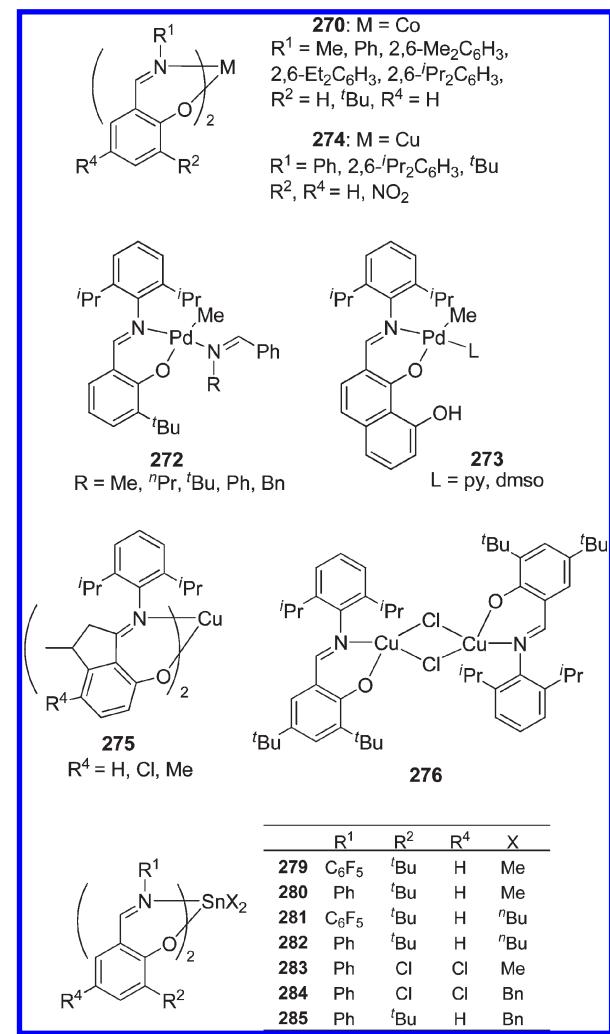
compared to the corresponding  $\text{R}^1 = \text{Ph}$  complex.<sup>242</sup> The V complex having imidazolium salts at  $\text{R}^1$  (264) gave linear PEs with large PDI values upon activation with MAO.<sup>211</sup> Nomura and co-workers synthesized arylimido-supported (phenoxy-imine) vanadium complexes,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})\text{V}(\text{L}^{\text{FI}})\text{Cl}_2$  (26–28), which adopted a distorted square pyramidal geometry with the imido at the apical position. Upon activation with MAO, the ethylene polymerization activities increased with the size of  $\text{R}^2$  substituents (<sup>t</sup>Bu > Me > H), and the activities of 28 ( $\text{R}^2 = \text{t}$ Bu) were substantially higher than those of the simple phenoxide,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})\text{V}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})\text{Cl}_2$ .<sup>244</sup>

An EPR study on vanadium complex 265 in combination with  $\text{R}_{(3-n)}\text{AlCl}_n$  ( $\text{R} = \text{Et}$  or  $\text{Me}$ ,  $n = 0$  or 1) with and without ETA suggested that the active species were V(IV) species and that ETA prevented reduction of the V(IV) species to V(III) species. These species were considered to be mono(phenoxy-imine) V(III or IV) species, where one of the phenoxy-imine ligands was lost by a ligand transfer reaction to alkylaluminums in a similar way as that observed for the group 4 metal complexes (see section 3.4). Any V(II) species were not observed under the conditions examined.<sup>519</sup>

The niobium and tantalum complexes (29 and 30) were isolated, and their solid state structures were determined but showed no ethylene polymerization activities.<sup>189</sup>

**4.3.3. Chromium Complexes.** Gibson and co-workers synthesized and characterized a bis(phenoxy-imine) Cr(III) complex 31, which adopted a distorted square pyramidal geometry with the chlorine or ethyl groups at the apical site.<sup>245</sup> The acetonitrile adduct of 266 adopted an octahedral *cis*-(Cl, MeCN) geometry (Scheme 28),<sup>88,245</sup> showing the possibility of an efficient olefin polymerization reaction. However, upon activation with  $\text{R}_2\text{AlCl}$  ( $\text{R}: \text{Et}, \text{Me}$ ), they were only moderately active in ethylene polymerization (30–100 g-polymer/(mmol-M·h·bar)).

Chart 19



A possibility that one of the phenoxy-imine ligands might be removed by an activator was suggested, although attempts to separately synthesize a monoligated  $(\text{L}^{\text{FI}})\text{CrCl}_2(\text{L})$  complex were unsuccessful with the ligands ( $R^1 = 2,6-\text{iPr}_2\text{C}_6\text{H}_3, R^2 = R^4 = ^t\text{Bu}$ ), which eventually led the authors to develop Cr complexes bearing a tridentate phenoxy-imine ligand that possessed a pendant donor at the  $R^1$  substituent (see section 5.3). Monoligated Cr complexes could be prepared in situ by using equimolar amounts of a phenoxy-imine ligand and  $(p\text{-tolyl})\text{CrCl}_2(\text{thf})_3$  as a metal source, and they were examined in ethylene polymerization.<sup>88,192,246</sup> For small  $R^1$  groups such as primary or secondary alkyls, these in situ generated complexes exhibited significant activities ( $>1000$  g-polymer/(mmol·M·h·bar)) with 9-anthracyl as  $R^2$ , while aryl  $R^1$  groups, particularly the 2,6-diisopropylphenyl group, showed a very low activity, where severe steric conflicts between the isopropyl groups and the chlorines in a tetrahedral framework were suggested.<sup>88</sup> The ligands bearing other  $R^2$  groups such as  $^t\text{Bu}$  or Ph exhibited poor performance even with  $R^1 = \text{isopropyl}$ , and the phenoxy-ketimine ligand ( $R^6 = \text{Me}$ ) generated a poor catalyst with  $R^1 = \text{isopropyl}$  and  $R^2 = 9\text{-anthracyl}$ , indicating a sensitivity of these substitution patterns to the polymerization activities.

The Cr bis-ligated complex **267** having imidazolium salts at  $R^1$  gave linear PEs with large PDI values upon activation with MAO.<sup>211</sup> Hybrid Cr complexes bearing  $\text{Cp}^*$  and a phenoxy-imine ligand,  $(\text{L}^{\text{FI}})(\text{Cp}^*)\text{CrCl}$  (**268**; Chart 18), were synthesized by Mu and co-workers.<sup>351</sup> These complexes demonstrated high activities for ethylene polymerization (up to 4 kg-polymer/(mmol·M·h·bar)) when activated with  $\text{R}_3\text{Al}$  and gave high molecular weight linear PEs ( $>10^6$  g/mol). Similar  $(\text{Cp}^*)(\text{phenoxy}-\text{ketylne})$  hybrids **269** were prepared by Jin and co-workers, demonstrating activities of 20–170 g-polymer/(mmol·M·h·bar).<sup>357</sup>

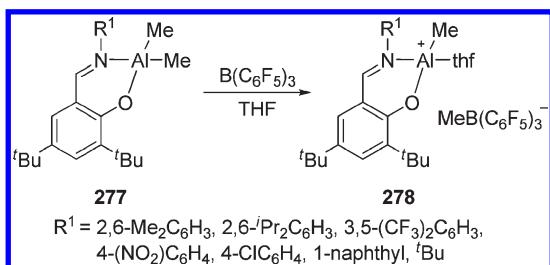
**4.3.4. Cobalt Complexes.** Cobalt (phenoxy-imine) complexes were applied to ethylene oligomerization and 1,3-butadiene polymerization. The phenoxy-2,6-diimine complexes (**223** in Chart 14) were examined for ethylene oligomerization in conjunction with MAO.<sup>260,263</sup> The complexes afforded  $\text{C}_4\text{--C}_6$  olefins, albeit at low efficiency: lower than that for the analogous nickel complexes (see section 4.2). Ethylene oligomerization using  $(\text{L}^{\text{FI}})_2\text{Co}/\text{EAO}$  (ethylaluminioxane) was investigated at high temperatures of 140–200 °C, giving  $\text{C}_4\text{--C}_{10}$  olefins (linear 1-alkene, 70–80%) in 30–160 g-oligomer/(mmol·M·h) at 1.5 MPa ethylene pressure.<sup>520</sup> Kim and co-workers revealed that bis-ligated Co complexes **270** (Chart 19) were better activated with  $\text{Et}_3\text{Al}_2\text{Cl}_3$  than MAO or  $\text{R}_3\text{Al}$  under mild conditions at 30 °C, affording 1-alkenes up to  $\text{C}_{20}$  with 1-butene as a major product in about 70% yield.<sup>256</sup> They also demonstrated that the complexes bearing bulky  $R^1$  and  $R^2$  tend to show higher activities, reaching to 179 g-oligomer/(mmol·M·h·bar). The same complexes were applied to 1,3-butadiene polymerization under similar conditions, which gave poly(butadiene) in about 50% yield with high 1,4-cis selectivity (94–98%). As  $R^1$  and  $R^2$  became bulkier, the selectivity slightly dropped.<sup>255</sup> In both cases, monoligated Co species were proposed to be an active species. A similar proposal was made by Endo and co-workers when they examined bridged and unbridged Schiff base Co complexes in 1,3-butadiene polymerization.<sup>254</sup>

**4.3.5. Palladium Complexes.** Despite the success of the Ni complexes, the analogous palladium complexes were less extensively investigated. Li and co-workers prepared three Pd complexes of the type  $(\text{L}^{\text{FI}})\text{PdMe}(\text{Ph}_3\text{P})$  (**271**) and examined NBE polymerization.<sup>332</sup> They showed lower activities than those of the Ni analogues,<sup>505</sup> and the obtained poly(NBE)s were insoluble in organic solvents. Sen and co-workers synthesized similar complexes having Schiff bases as a neutral donor,  $(\text{L}^{\text{FI}})\text{PdMe}(\text{Ph}-\text{CH}=\text{N}-\text{R})$  (**272**), which were inactive in ethylene, propylene, and NBE polymerizations, presumably due to insufficient lability of the nonchelated imine donors.<sup>333</sup> Recently, Sen and co-workers prepared and characterized  $(\text{L}^{\text{FI}})\text{PdMe}(\text{L})$  (**273**) having a naphthalene-1,8-diol scaffold ( $\text{L}$ : dmsO, pyridine).<sup>521</sup> The complexes afforded branched low molecular weight PEs at very low to low activity, but when NBE (bearing functional groups) was added, the polymerization proceeded in a living manner.

Ziegler and co-workers conducted some theoretical studies on the phenoxy-imine Pd complexes, in which they suggested that ethylene copolymerization with N-containing polar comonomers might be possible.<sup>522–524</sup>

**4.3.6. Copper Complexes.** Bis(phenoxy-imine) or bis(phenoxy-ketylne) Cu complexes **274** and **275** were employed in polymerization of ethylene, NBE, and MMA and copolymerization of ethylene with MMA, where a Cu(I) mediated insertion mechanism was proposed.<sup>335,336,525,526</sup> For

Scheme 29

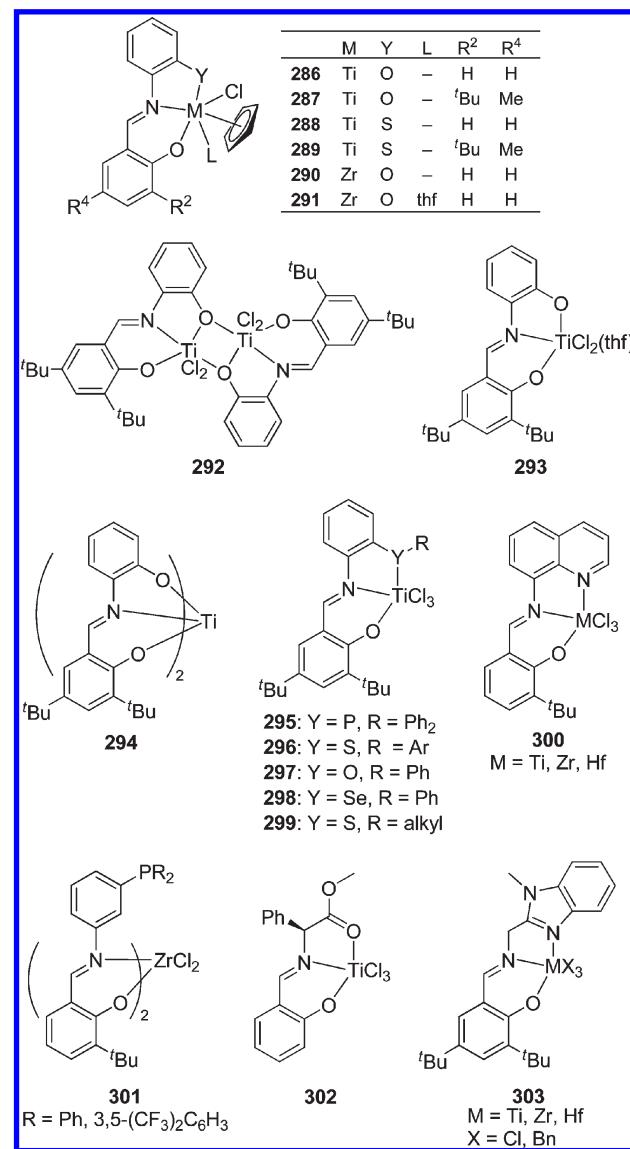


example, complex ( $R^1 = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3, R^2 = R^4 = \text{NO}_2$ ) with MAO polymerized NBE into high molecular weight 1,2-addition type polymers with relatively small PDI values. On the other hand, prevailingly syndiotactic high molecular weight poly(MMA)s with large PDI values were obtained by the same catalyst systems. Ethylene homopolymerization with the  $(L^{\text{FI}})_2\text{Cu}/\text{MAO}$  afforded high molecular weight linear PEs. In the copolymerization of ethylene and MMA, the crude products again with large PDI values apparently included 70–90 mol % MMA units. In all cases, the activities were mostly very low in  $<10$  g-polymer/(mmol-M·h). Foley and co-workers demonstrated that, under the conditions,  $(L^{\text{FI}})_2\text{Cu}$  (274) or related Cu complexes 276 formed  $(L^{\text{FI}})\text{AlMe}_2$  in the presence of MAO and that the Al complexes showed very similar ethylene polymerization characteristics even in the absence of the Cu complexes.<sup>337</sup> Combined with the possible involvement of radical species, the results appeared to accommodate the often observed multisited characteristics.

**4.3.7. Aluminum Complexes.** Due to a wide variety of chemical transformations mediated by neutral and cationic alkylaluminum coordination complexes, the research on alkylaluminum chelate complexes has been intense. Ethylene insertion into Al–C bonds of  $\text{Et}_3\text{Al}$  at high temperatures is the very root of Ziegler catalysis, and recently, it has been revealed that ethylene insertion took place under mild conditions with cationic alkylaluminum complexes with low coordination numbers.<sup>527–531</sup> With regard to phenoxy–imine complexes, phenoxy–imine Al complexes can be formed in situ via a ligand transfer reaction from a transition metal (phenoxy–imine) complex to alkylaluminums added as a cocatalyst, as discussed on several occasions in this review (see sections 3.2.1, 3.4, 3.5, and 4.1.2.4). However, there were a few examples where the discrete Al complexes were isolated and characterized, and then tested in ethylene polymerizations. Gibson and co-workers synthesized and characterized a series of monoligated phenoxy–imine Al complexes 277 by a simple methane elimination protocol between  $(L^{\text{FI}})\text{H}$  and  $\text{Me}_2\text{Al}$ .<sup>340</sup> Upon addition of  $\text{B}(\text{C}_6\text{F}_5)_3$ , the cationic species,  $[(L^{\text{FI}})\text{AlMe}(\text{thf})]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  (278), were obtained as analytically pure forms in the presence of THF (Scheme 29). In the absence of THF molecules, the reaction mixtures are complex and  $\text{C}_6\text{F}_5$  transfer was observed, which resulted in the formation of  $(L^{\text{FI}})\text{AlMe}(\text{C}_6\text{F}_5)$  and  $\text{MeB}(\text{C}_6\text{F}_5)_2$ . Pappalardo and co-workers carried out similar experiments to generate  $[(L^{\text{FI}})\text{AlMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ , which consumed ethylene in NMR tubes. The species could also be trapped by added THF. These Al cationic species (THF free) showed very low activities for ethylene polymerization at  $<1$  g/(mmol-M·h·bar),<sup>341</sup> which was in accordance with the results obtained by Foley, as discussed in section 4.3.6.

**4.3.8. Tin Complexes.** Pappalardo and co-workers synthesized  $(L^{\text{FI}})_2\text{SnX}_2$  ( $X = \text{alkyl}$ ) complexes 279–285 and investigated

Chart 20

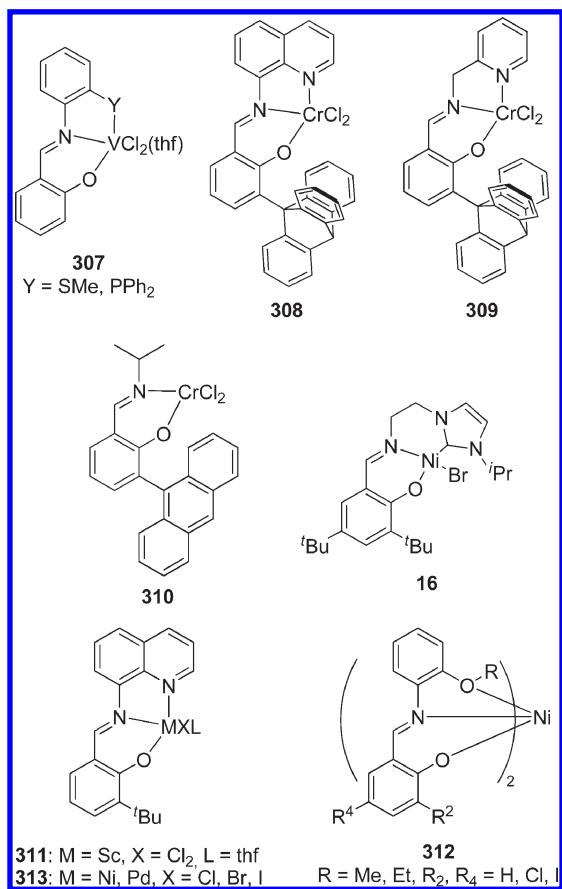


them as ethylene oligomerization catalysts.<sup>343,344</sup> Complexes with a perfluorophenyl group on the  $R^1$  (279, 281) only afforded mixtures of decomposition products in the presence of ionizing reagents, such as  $[(\text{C}_6\text{H}_5)\text{NH}(\text{CH}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and  $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . On the other hand, non-fluorinated complexes 280 and 282 formed cationic species through alkyl abstraction by borate compounds. Compound 285 in combination with  $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , and compounds 283 or 284 in combination with  $\text{B}(\text{C}_6\text{F}_5)_3$  were able to oligomerize ethylene under mild conditions, giving oligomers with saturated end groups and methyl branches.

## 5. POLYMERIZATION WITH TRIDENTATE PHENOXY–IMINE COMPLEXES

Tridentate phenoxy–imine ligands that have another pendant donor at the  $R^1$  group are easily accessible using primary amines having functional groups at suitable positions in the Schiff base condensation with salicylaldehydes. These tridentate

Chart 21



phenoxy-imine ligands ( $L^{FI}-L$  or  $L^{FI}-X$  for monoanionic and dianionic ligands, respectively) can be used effectively for creating an appropriate environment around the coordination sphere of the metal complexes by sterically and electronically adjusting the coordination number and charge of the metal complexes. Monoanionic tridentate ( $L^{FI}-L$ ) ligands that can stabilize a complex with lower coordination numbers and lower electron counts better than two phenoxy-imine ligands are particularly useful because these ligands secure a wider space for incoming substrates, while keeping the electrophilicity as high as that of a mono-( $L^{FI}$ ) complex.

### 5.1. Group 4 Metal Complexes

In an attempt to prepare ( $Cp$ )( $L^{FI}$ ) hybrid complexes by Qian and co-workers, a tridentate phenoxy-imine ligand that has an *ortho*-methoxyphenyl group as  $R^1$  was employed, which resulted in a dianionic diphenoxide (**286**), presumably via an intramolecular O–Me bond activation.<sup>104</sup> The complex showed low activities in ethylene polymerization and ethylene/1-hexene copolymerization, affording high molecular weight (co)polymers ( $M_w 10^5-10^6$  g/mol) but with somewhat large PDI (~5). Later, Jin and co-workers synthesized this type of complex in a series (**286–290**) and examined ethylene polymerization, which showed somewhat improved activities of 10–150 g-polymer/(mmol-M·h·bar).<sup>103</sup> The sulfur pendant donor (vs oxygen),  $R^2 = {^t}Bu$  (vs H), and the Zr metal center (vs Ti) tended to show higher polymerization activities. Huang and co-workers reported on the synthesis of similar hybrid Zr complexes and their ethylene

(co)polymerization behavior.<sup>102,106</sup> The Zr complex **291** appeared to show higher activity (272 g-polymer/(mmol-M·h·bar)) than the Ti analogues. A low level of 1-hexene uptake in copolymerization with ethylene was also reported.<sup>106</sup>

Ladipo and co-workers employed a tridentate phenoxy-imine ligand that has an *ortho*-hydroxyphenyl group as  $R^1$  and obtained similar complexes in a dimer, ( $L^{FI}-O$ )<sub>2</sub>Ti<sub>2</sub>Cl<sub>4</sub> (**292**; Chart 20), or a monomer, ( $L^{FI}-O$ )TiCl<sub>2</sub>(thf) (**293**), or a bis-ligated complex, ( $L^{FI}-O$ )<sub>2</sub>Ti (**294**), none of which were examined for polymerization.<sup>101</sup> Jin and co-workers used alternatively anionic sulfur as a pendant donor of aryl  $R^1$  to synthesize ( $L^{FI}-S$ )TiX<sub>2</sub> (X: Cl, O*i*Pr).<sup>107</sup> Ethylene polymerization tests exhibited activity up to 1.2 kg-polymer/(mmol-M·h·bar). The activities appeared to increase with the size of  $R^2$ :  ${^t}Bu > Me > H$ . The bis-ligated complexes ( $L^{FI}-S$ )<sub>2</sub>Ti were inactive for ethylene polymerization.

There have been more examples that reported on the complexes bearing neutral pendant donors, ( $L^{FI}-L$ )TiX<sub>3</sub>, particularly bearing soft donors such as sulfur and phosphorus. Tang and co-workers synthesized such a complex that possessed 2-(PPh<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub> as  $R^1$ .<sup>109</sup> The bis-ligated complexes, ( $L^{FI}-PPh_2$ )<sub>2</sub>TiCl<sub>2</sub>, showed little ethylene polymerization activity; however, mono-ligated ( $L^{FI}-PPh_2$ )TiCl<sub>3</sub> (**295**) exhibited appreciable activities in ethylene polymerization (up to 1.41 kg-polymer/(mmol-M·h·bar)) and copolymerization with 1-hexene and NBE, providing high molecular weight (co)polymers ( $M_w 10^4-10^5$  g/mol) with small PDI values ( $M_w/M_n 2-3$ ). Presumably because the five-coordinated complex can be less sterically crowded, the comonomer uptakes were high and a positive comonomer effect was observed for ethylene/1-hexene copolymerizations.

Within this context, a variety of similar sulfur coordinated Ti complexes ( $L^{FI}-SAr$ )TiCl<sub>3</sub> (**296**) were examined in ethylene (co)polymerizations in order to establish the effects of the neutral donors (O, S, Se) and the substituted S-aryl groups (Ar: Ph, 4-(CF<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>, 4-(OMe)C<sub>6</sub>H<sub>4</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, etc.).<sup>113,114</sup> When activated with MMAO, these complexes exhibited ethylene polymerization activities up to 3.98 kg-polymer/(mmol-M·h·bar) ( $M_w 2.96 \times 10^4$  g/mol) (complex **296**, Ar = Ph), which was far higher than that of the complex bearing an oxygen donor (0.032 kg-polymer/(mmol-M·h·bar), complex **297**), demonstrating the beneficial effects of the S donors. The analogous complex that possessed an Se donor (**298**) afforded a higher molecular weight PE ( $M_w 5.01 \times 10^4$  g/mol) in somewhat lower activity (2.38 kg-polymer/(mmol-M·h·bar)). The electronic effects on Ar groups were not apparent, but 2,6-dialkyl substitution at Ar deteriorated the polymerization activities significantly, although the molecular weights of the obtained polymers were increased. The alkylthio groups were also examined for the tridentate ligand framework, ( $L^{FI}-SR$ )TiCl<sub>3</sub> (**299**, R: Me, *i*Pr, *n*Pr, *t*Bu, *n*-octyl, *n*-octadecyl).<sup>532</sup> These complexes exhibited comparable ethylene polymerization activities to that of the ( $L^{FI}-SPh$ )TiCl<sub>3</sub>, except for the complex that possessed a S-*t*Bu group as a pendant donor, indicating again the importance of the steric effects. Accordingly, this complex showed a lower activity and a higher molecular weight capability.

These complexes were successfully applied to the copolymerization of ethylene with  $\alpha$ -olefins, cyclic olefins such as NBE or dicyclopentadiene (DCPD), and  $\alpha$ -olefinic polar monomers having masked functional groups at the  $\omega$ -position, taking advantage of their steric openness relative to bis-ligated complexes.<sup>115,116,532,533</sup> Again, the steric effects of the sulfur donors were prominent; that is, the S donors with sterically

encumbered groups tended to result in lower activities, lower comonomer uptakes, and productions of higher molecular weight polymers. It was demonstrated that these tridentate [O, N, S] phenoxy-imine ligands as well as related  $\beta$ -ketoimine ligands could be applied to a one pot screening protocol, where an equimolar mixture of a ligand and  $TiCl_4(\text{thf})_2$  was activated by MMAO in the presence of ethylene, in order to quickly identify promising ligand structures.<sup>180</sup>

Pellecchia and co-workers synthesized group 4 metal complexes bearing a phenoxy-imine ligand that possessed 8-quinoline as the R<sup>1</sup> substituent, which served as a monoanionic tridentate ligand to afford the complexes ( $L^{\text{FI}}-\text{N}$ ) $MCl_3$  (M: Ti, Zr, Hf) (300).<sup>100</sup> The activities in ethylene polymerizations were rather low, and the polymers showed very large PDI values. For propylene polymerizations, slightly isotactic-rich polypropylenes were obtained from the Ti complex, nearly atactic from the Zr complex, and the Hf complex was barely active. Bochmann and co-workers reported the synthesis and characterization of the bis-ligated complexes bearing another phosphorus containing ligand (3-(PR<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> as R<sup>1</sup>, 301). The solid state structures of the bis-ligated complexes demonstrated the noncoordinating nature of the phosphorus donors, and apparently no significant effects of the pendant donors were observed in polymerization characteristics.<sup>221</sup> Erker and co-workers synthesized tridentate phenoxy-imine ligands using amino acid esters in Schiff base condensation. The titanium complexes (( $L^{\text{FI}}$ -COOMe) $TiCl_3$  (302), etc.) can be prepared where the carbonyl oxygen was bound to the titanium, although the polymerization was not

investigated.<sup>111</sup> Gibson and co-workers synthesized complexes that possessed a 1-methyl-2-benzimidazolylmethyl group as R<sup>1</sup> (( $L^{\text{FI}}-\text{L}$ ) $MX_3$ , M: Ti, Zr, Hf; X: Cl, CH<sub>2</sub>Ph, 303).<sup>112</sup> Only ( $L^{\text{FI}}-\text{L}$ ) $TiCl_3/\text{Bu}_3\text{Al}/\text{DMAO}$  showed the ethylene polymerization activities of 150 g-polymer/(mmol-M·h·bar), but the PDI values of the obtained polymers were extremely large (~48).

Recently, Fujita and co-workers took a new turn regarding the tridentate phenoxy-imine ligated titanium complexes, which served, upon activation with MAO, as selective ethylene trimerization catalysts with extremely high activities.<sup>534,409</sup> The tridentate ligands were characterized by the 2'-alkoxy-biphenyl-2-yl groups as R<sup>1</sup> substituents (304–306), and thereby, the tridentated ligands wrapped around the Ti center in a facial fashion, in contrast to the meridional configurations of the complexes so far discussed above (Figure 10). As summarized in Table 33, complex 306 selectively produced 1-hexene in high activities (92.3%, 315 kg-1-hexene/(mmol-M·h) at 5.0 MPa ethylene pressure), in which branched decenes (7.3%, cotrimerization products of 1-hexene and two molecules of ethylene) and a small amount of PE (0.4%) were the byproducts. The activities were 2 orders of magnitude higher than those of commercial Cr-based catalysts (Phillips catalyst) under comparable conditions. A mechanism was proposed where oxidative addition of two ethylene molecules to Ti(II) species formed a Ti(IV) metallacyclic species, and insertion of another ethylene to the species led to a metallacycloheptane intermediate, which was subject to  $\beta$ -H elimination/transfer and reductive elimination in a stepwise or concerted manner to regenerate the Ti(II) species (Scheme 30). The pendant OMe donor was considered to stabilize the Ti(II)

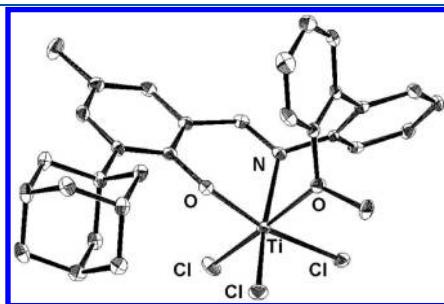


Figure 10. Molecular structure of complex 306. Reproduced with permission from ref 534. Copyright 2010 American Chemical Society.

Scheme 30

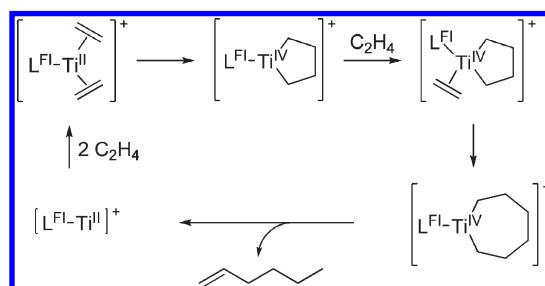
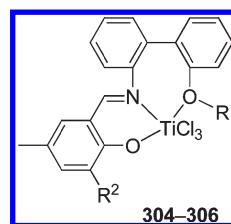


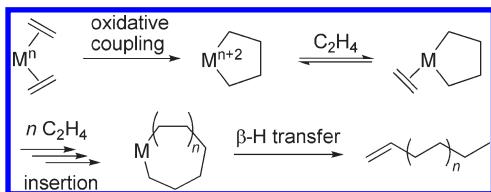
Table 33. Catalytic Ethylene Conversion with the Tridentate Phenoxy-Imine Ti Complexes<sup>a</sup>



complex	R	$R^2$	$C_2H_4$ pressure (MPa)	activity [kg-hexene/(mmol-M·h)]	selectivity (wt %)		
					$C_6$	$C_{10}$	PE
304	Ph	CMe <sub>2</sub> Ph	0.8	0.19	76.6	0	23.4
305	Me	CMe <sub>2</sub> Ph	0.8	5.7	86.2	12.2	1.6
306	Me	1-adamantyl	0.8	7.4	91.4	6.4	2.1
306 <sup>b</sup>	Me	1-adamantyl	5.0	315	92.3	7.3	0.4

<sup>a</sup> Conditions: cyclohexane, 30 mL; complex, 0.5  $\mu\text{mol}$ ; MAO, 5.0 mmol; 30 °C; 1 h. <sup>b</sup> Cyclohexane, 150 mL.

Scheme 31



species. The reaction demonstrated second order dependence on ethylene pressure, indicating that formation of the metallacyclopentane intermediate can be the rate-determining step, which is in contrast to the cases of similar cyclopentadienyl-arene titanium complexes, which showed an apparent first order dependence on the ethylene concentration in the ethylene trimerization reaction.<sup>535</sup>

## 5.2. Vanadium Complexes

As discussed in section 4.3.2, mono- and bis(phenoxy-imine) ligated vanadium complexes that showed high activities in ethylene polymerization were accessible, although those complexes, especially monodentate ones, suffered from thermal instability in polymerizations at higher temperatures.<sup>240</sup> Aiming at improving the thermal stability, Li and co-workers introduced tridentate phenoxy-imine ligands onto the vanadium complexes,  $(L^{FI}-L)VCl_2(\text{thf})$ .<sup>98</sup> It was revealed that soft donors ( $-SMe$  and  $-PPh_2$ ) complexes 307; Chart 21) provided the catalysts with stable reaction profiles for longer periods and narrower PDI values even at higher polymerization temperatures. Copolymerizations of ethylene with 1-hexene or NBE were also examined with these complexes, resulting in appreciable comonomer incorporations.

## 5.3. Chromium Complexes

As discussed in section 4.3.3, Gibson and co-workers demonstrated that monoligated complexes  $[(L^{FI})CrCl_2(L)_n]$  that possessed small  $R^1$  and bulky  $R^2$  substituents were significantly more active in ethylene polymerization than bis-ligated complexes  $[(L^{FI})_2CrCl(L)_n]$ . This lead discovery was subsequently applied to an extensive ligand library of salicylaldimine bearing a variety of  $R^1$  and  $R^2$  substituents, which included tridentate ligands. As a result, unique tridentate Cr complexes 308 and 309, which exhibited high activities for ethylene polymerization and oligomerization, were identified by means of a high throughput screening method.<sup>88,96,246,409</sup> The activities reached as high as 10 kg-polymer/(mmol-M·h·bar) for polymerization. Kirillov, Carpentier, and their co-workers synthesized related Cr(III) complexes and examined ethylene oligomerization using MAO as a cocatalyst.<sup>86</sup>

The oligomerization with these Cr catalysts was proved to take place via metallacyclic species, in contrast to the Cossee-Arlman chain growth mechanism commonly seen for other metal-mediated polymerizations (Scheme 31), since cooligomerization of an equimolar  $C_2H_4/C_2D_4$  mixture did not show the H/D scrambling that was postulated for the Cossee-Arlman mechanism.<sup>536,537</sup> The oligomerization catalyst 308 bearing a tridentate phenoxy-imine ligand in the presence of  $Et_2Zn$  gave molecular weight distributions closed to Poisson statistics rather than Schulz-Flory, which indicated rapid and reversible chain transfer (relative to chain growth) to alkylzinc species (catalytic chain growth on zinc), although the fast  $\beta$ -H transfer caused

deviation from the pure Poisson distributions.<sup>538</sup> The bidentate Cr catalyst 310 showed statistics rather close to Schulz-Flory distributions.

## 5.4. Complexes with Other Metals

Longo and co-workers prepared a Sc complex bearing an 8-quinolinyl  $R^1$  group as a pendant donor (311). The complex with MAO was employed in ethylene and 1,3-butadiene homopolymerization and afforded linear PE in a very low activity ( $M_w 6.3 \times 10^5$  g/mol,  $M_w/M_n 1.9$ ) and 1,4-cis rich polybutadiene (86%), respectively.<sup>140</sup> Yasuda and co-workers used iron complexes bearing a 2-pyridylmethyl group as  $R^1$  ( $R^2 = R^4 = ^t\text{Bu}$ ) along with other polydentate N-donor ligands for polymerization of isoprene and 1,3-butadiene. Upon activation with MMAO, the complexes gave polymers having low PDI values (2–3) in nearly quantitative yields, although the microstructural selectivity was not great.<sup>97</sup> Shen and co-workers synthesized a Ni complex supported by a tridentate ligand bearing NHC as a pendant donor,  $(L^{FI}-\text{NHC})\text{NiBr}$  (16), and examined styrene polymerization with  $\text{NaB}(C_6F_5)_4$ .<sup>117</sup> Sun and co-workers prepared bis-ligated complexes,  $(L^{FI}-L)_2\text{Ni}$  (312 L: 2-(RO) $C_6H_4$ ), which were active in NBE polymerization, with MAO activation as high as 804 g-polymer/(mmol-M·h·bar).<sup>105</sup> Ni and Pd complexes bearing 8-quinolinyl  $R^1$  (313) were examined by Chen and co-workers for NBE polymerization.<sup>99</sup> Large solvent effects were revealed, and the activity reached 47.6 kg-polymer/(mmol-M·h·bar) in dichloromethane. The Pd analogues exhibited somewhat lower activities for NBE polymerization but gave higher molecular weight polymers. The Pd complex that possessed a  $Ph_2P$ -pendant donor showed no activity in ethylene polymerization in its neutral or cationic (acetonitrile coordinated) form.<sup>108</sup> Gibson and co-workers synthesized Al complexes,  $(L^{FI}-L)\text{AlMe}_2$ , generated a cationic species by adding  $B(C_6F_5)_3$ ,  $[(L^{FI}-L)\text{AlMe}]^+[MeB(C_6F_5)_3]^-$ , and examined ethylene polymerizations with the species, which afforded PEs in very low activities (50–110 mg-polymer/(mmol-M·h·bar)).<sup>339</sup>

## 6. POLYMERIZATION WITH TETRADENTATE [O,N,N,O] PHENOXY-IMINE COMPLEXES

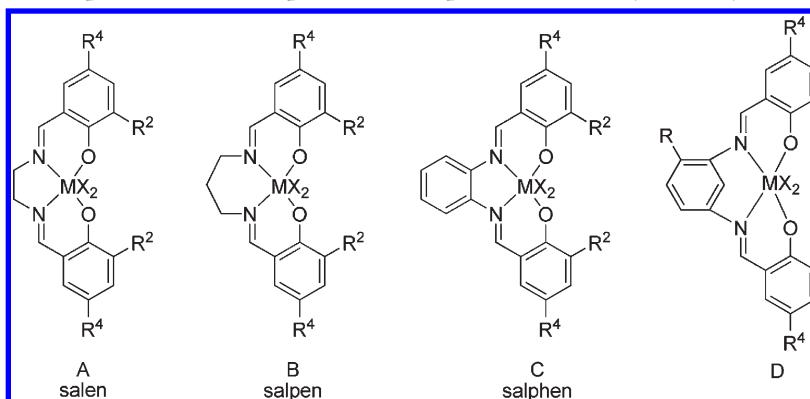
Historically, tetradentate Schiff base ligands represented by salen, salphen, and their derivatives have been used as an organometallic catalyst in combination with a variety of metals, particularly as an asymmetric catalyst for an oxidation reaction.<sup>539–541</sup> In this section, the olefin polymerization catalysts supported by the tetradentate bridged phenoxy-imine ligands ( $L^{FI-FI}$ ), including the ones that possessed bridging groups other than salen or salphen, will be discussed with respect to each metal.

### 6.1. Group 4 Metal Complexes

As mentioned in section 3.1.1, those traditional Schiff base ligands such as salen and salphen tend to adopt the geometry *cis*-N/*cis*-O/*trans*-X with group 4 metals,<sup>174,175,209,359,360,542–547</sup> whereas in order for efficient olefin insertion to occur, the X ligands (potential reaction site) are preferably placed *cis* to each other.

Among the phenoxy-azo and phenoxy-imine chelating compounds, which Taylor screened for ethylene polymerization in conjunction with  $TiCl_4/Et_2AlCl$  (see section 1.1), bridged phenoxy-imine ligands, salen, salphen, and salphen, were examined, but they were considered to be inactive (rather correctly in retrospect).<sup>34</sup> The investigation on group 4 metal complexes of

Table 34. Salen, Salpen, and Salphen Related Group 4 Metal Complexes for the Ethylene Polymerization Catalysts

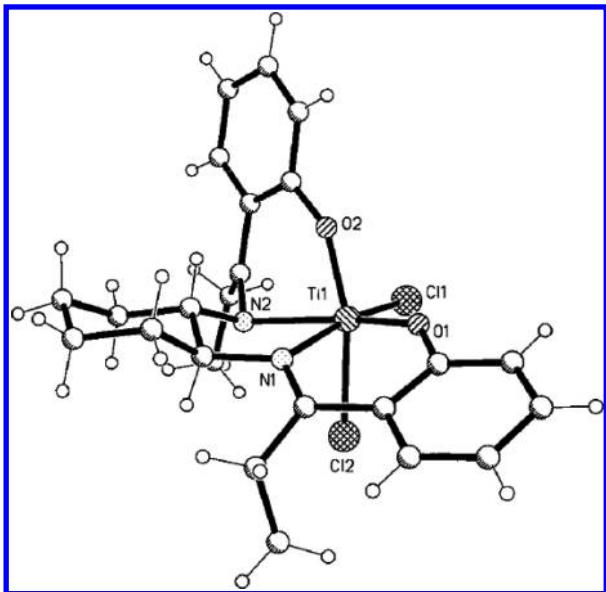


complex	M	X	R <sup>2</sup>	R <sup>4</sup>	R	ref
A	Ti	Cl	H	H		176, 548
A	Ti	Cl	OMe	H		176
A	Ti	Cl	OEt	H		176
A	Ti	Cl	tBu	tBu		176
A	Ti	Cl	H	Cl		176
A	Ti	Cl	H	Br		176
A (314)	Zr	Cl	H	H		209, 228, 361, 548
A	Zr	Cl	tBu	tBu		209, 228
A	Zr	Cl	H	OMe		209
A	Zr	Cl	H	Cl		209
A	Zr	Cl	H	NO <sub>2</sub>		209
A	Zr	Cl	OMe	H		176
B (315)	Ti	Cl	H	tBu		178
B (316)	Ti	Cl	tBu	H		178
B (317)	Ti	Cl	Me	H		178
C (41)	Ti	Cl	H	H		169
C	Ti	Cl	tBu	tBu		228, 547
C	Zr	Cl	H	H		169, 209, 228
C (318)	Zr	Cl	tBu	tBu		209, 225
C	Zr	Cl	H	OMe		209
C	Zr	Cl	H	Cl		209
D	Ti	O <i>i</i> Pr	H	H	H	125, 197
D	Ti	O <i>i</i> Pr	H	OMe	H	125, 197
D	Ti	O <i>i</i> Pr	H	Br	H	125, 197
D	Ti	O <i>i</i> Pr	H	OMe	Me	125, 197
D	Ti	O <i>i</i> Pr	H	H	Me	197, 125
D	Ti	O <i>i</i> Pr	H	Br	Me	125, 197
D	Ti	O <i>i</i> Pr	H	tBu	Me	197
D	Ti	O <i>i</i> Pr	H	Me	H	125, 197
D	Ti	O <i>i</i> Pr	H	Cl	H	125, 197
D	Ti	O <i>i</i> Pr	H	tBu	H	125
D <sup>a</sup>	Zr	O <i>i</i> Pr	H	H	H	125, 234
D <sup>a</sup>	Zr	O <i>i</i> Pr	H	OMe	H	125, 234
D <sup>a</sup>	Zr	O <i>i</i> Pr	H	tBu	Me	234
D <sup>a</sup>	Zr	O <i>i</i> Pr	H	H	Me	125, 234
D <sup>a</sup>	Zr	O <i>i</i> Pr	H	tBu	H	125

<sup>a</sup> The dimer structure is proposed.

salen, salpen, or salphen for olefin polymerization was resumed after a long pause in the late 1990s, which is compiled in Table 34.<sup>123,169,176,178,197,209,225,228,234,361,547,548</sup> Repo and co-

workers prepared a Zr salen complex, ( $\text{L}^{\text{FI}-\text{FI}}$ ) $\text{ZrCl}_2(\text{thf})$  (314), and determined their solid state structures by X-ray crystallography, which revealed that the chlorides were trans to each



**Figure 11.** Molecular structure of **319**. Selected bond lengths (Å) and angles (deg): Ti(1)–O(1), 1.796(5); Ti(1)–O(2), 1.827(5); Ti(1)–N(1), 2.186(5); Ti(1)–N(2), 2.205(6); Ti(1)–Cl(1), 2.323(2); Ti(1)–Cl(2), 2.391(3); O(1)–Ti(1)–O(2), 99.5(2); N(1)–Ti(1)–N(2), 76.6(2); N(2)–Ti(1)–Cl(1), 99.67(16); Cl(1)–Ti(1)–Cl(2), 86.89(9). Reproduced with permission from ref 40. Copyright 1999 Royal Society of Chemistry.

other and the THF molecule occupied the seventh coordination site in the ONNO plane.<sup>361</sup> The *trans*-Cl atoms of some Zr and Hf acen complexes were rearranged *cis* to each other upon removal of the THF molecule,<sup>546</sup> however, the Zr salen complex exhibited similar low activities (120–130 g-polymer/(mmol-M·h) at 80 °C, 0.5 MPa) with and without the coordinated THF. Likewise, these salen or salphen complexes appeared to adopt the *trans*-X configuration and thereby showed low to modest activities for ethylene polymerization. There is one report in which it is suggested that a ( $L^{FI-FI}$ ) $ZrCl_2$  (**318**) existed as two isomers in solution in equilibrium and that the minor component was a *cis*-Cl isomer.<sup>225</sup> Jin examined (salpen) $TiCl_2$  complexes (**315**–**317**: C<sub>3</sub>-linkage) with varied phenolic alkyl substituents for ethylene polymerization. The chlorines were *trans* to each other (Cl–Ti–Cl angle: 165.23(8)°), and the activities were in the range 351–414 g-polymer/(mmol-M·h·bar) (cocatalyst: MAO).<sup>178</sup>

To overcome this intrinsic problem associated with the salen, salpen, and salphen framework, while keeping the rigid and possibly chiral environments around the metal center, modifications of the bridging moiety have been investigated so that the X ligands can have the desired *cis* disposition.

Bis(phenoxy–ketimine) ligands having a *trans*-1,2-cyclohexylene bridge afforded complex **319** or **320** with *cis*-N/*cis*-O/*cis*-Cl geometry with a titanium center (Cl–Ti–Cl angle is 86.9(1)°) (Figure 11).<sup>40</sup> The complexes exhibited an ethylene polymerization activity with MAO (20–100 g-polymer/mmol-M·h), which is higher than those of analogous *trans*-X complexes. Using the same linkage, tetradeinate bis(phenoxy–imine) Zr complexes **321** and **322** were prepared, whose geometries are *cis*-N/*trans*-O/*cis*-X or mixtures with *cis*-N/*cis*-O/*cis*-X, depending on X (Cl or benzyl).<sup>42</sup> They showed activities for ethylene polymerization similar to those of the complex above.

Tetradeinate bis(phenoxy–imine) ligands possessing a 2,2'-biaryl bridge gave a *C*<sub>2</sub>-symmetric *cis*-N/*trans*-O/*cis*-X complex **323** (see also section 3.1.1).<sup>41,149,151,152,226,227</sup> The complexes that possessed R<sup>5</sup> = Me (adjacent to –CH=NR<sup>1</sup>), which was introduced to circumvent the 1,2-migratory insertion of the Zr-bound benzyl group, showed low activity toward ethylene polymerization (45–60 g-polymer/(mmol-M·h·bar)), while the complex without the R<sup>5</sup> substituent exhibited no activities under the same conditions.<sup>227</sup>

The Zr and Ti complexes supported by tetradeinate ligands having a similar binaphthyl bridge (**324**; Chart 22) were prepared by Pellecchia and co-workers.<sup>43,229,230,462</sup> The configurational geometries were crystallographically identified as *cis*-N/*trans*-O/*cis*-Cl for the Zr complex and *cis*-N/*cis*-O/*cis*-Cl for the Ti analogue. All these complexes showed very low to low activities, particularly when *t*Bu<sub>3</sub>Al was not added. Together with very large PDI values and formation of phenoxy–amine ligands by hydrolysis experiments, the active species were considered to be reduced at the imine functions (see also section 4.1.2), which was confirmed by the separate synthesis of the phenoxy–amine ligated complex.<sup>230</sup> This reduced phenoxy–amine species afforded isotactic poly( $\alpha$ -olefin)s, whose isotacticity became higher when longer 1-alkenes were applied. As anticipated, enantioselective isospecific polymerization of 4-methyl-1-hexene was possible when using each of the enantiometrically pure complexes.<sup>549</sup>

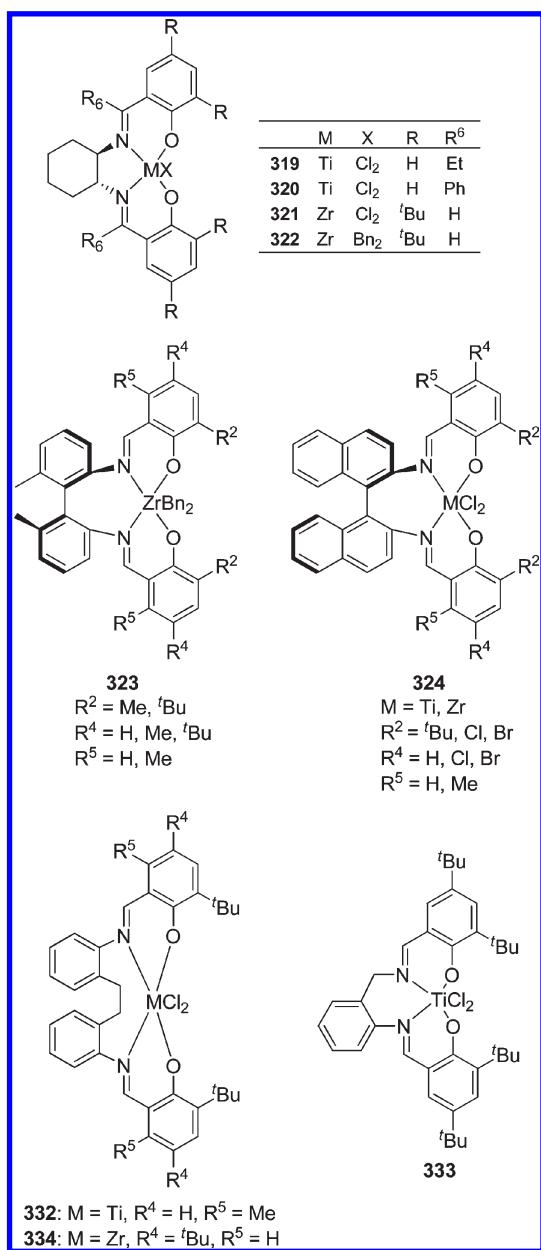
In any case, the activities for nonbridged complexes were far greater than those for the similar bridged complexes, despite the apparently similar chemical functionalities and *cis*-X geometries of these complexes. As discussed in section 3.1.1, this large difference will be primarily attributable to the constraints imposed by the bridged structures, which were explicitly demonstrated by the differences in structural parameters, such as the N–M–N and O–M–O angles within the same general *cis*-N/*trans*-O/*cis*-X.<sup>152</sup>

Fujita and co-workers took a simple approach to release the constraints associated with the bridged Schiff base complexes **325**–**331** by extending the length of the bridge. When the numbers of methylene groups between the two imine nitrogens reached 5 or 6, complexes **328**, **329**, and **331** exhibited significantly higher activities than those which had shorter linking chains (up to 9.1 kg-polymer/(mmol-M·h·bar) at 25 °C) (Table 35).<sup>210</sup> The calculations suggested that the procatalysts having the C<sub>6</sub>-linkage favored the *cis*-Cl geometry, while those which had shorter linkages favored the *trans*-Cl configuration. The highly active C<sub>6</sub>-linked complex **331** exhibited higher activities at higher polymerization temperatures (104 kg-polymer/(mmol-M·h·bar) at 75 °C), implying improved thermal stability due to the linked structures. Moreover, under commercially relevant solution conditions (150 °C, 3 MPa ethylene), complex **331** exhibited an activity of 143 kg-polymer/(mmol-M·h).

Gibson and co-workers also synthesized Ti and Zr complexes having bridged structures with different lengths.<sup>193</sup> Again, a C<sub>6</sub>-bridged structure combined with a Ti metal center provided a highly active single site catalyst (**332**, 2.6 kg-polymer/(mmol-M·h·bar) at 25 °C). The Zr counterpart showed lower activities and gave PEs with bi- or trimodal molecular weight distributions. Complex **333** adopted a *trans*-Cl geometry, and complex **334** showed a *cis*-Cl geometry with considerable ring strain. Neither of them furnished the ethylene polymerization catalysts when activated with MAO.

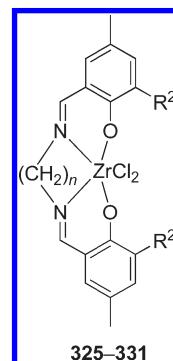
Meanwhile, Repo and co-workers suggested that the observed activity differences between bridged and nonbridged complexes can be solely attributed to the difference in the configurational geometry of the activated complex, where they assumed that the *trans*-N/*cis*-O/*cis*-(reaction sites) complex might be the most

Chart 22



active form based on calculations.<sup>44</sup> Bialek and co-workers suggested that the differences between bridged and nonbridged ligands in their polymerization characteristics were rather small when Ti or V salphen complexes were activated with EtAlCl<sub>2</sub> or Et<sub>2</sub>AlCl, which gave high molecular weight PEs with rather large PDIs or oligomers.<sup>169,176</sup> When Zr salen or salphen complexes were activated with Et<sub>2</sub>AlCl, they also became ethylene oligomerization catalysts.<sup>209,228</sup>

(Cp)(phenoxy-imine) hybrid complexes, (Cp)(L<sup>FI-FI</sup>)ZrCl or (Cp)(L<sup>FI</sup>)<sub>2</sub>ZrCl, were prepared and examined for ethylene polymerization with MAO.<sup>350</sup> Since these complexes had only one chlorine, cleavage of one of the Zr—O bonds was postulated. Nevertheless, the nonbridged complex exhibited significantly higher activities than the bridged complex. Walther and co-workers prepared a series of bridged Schiff base Zr complexes and examined polymerization of 1,5-hexadiene, which gave low

Table 35. Ethylene Polymerization Results with the Tetradentate Phenoxy–Imine Zr Complexes<sup>a</sup>

complex	<i>n</i>	R <sup>2</sup>	activity [kg-polymer/(mmol·M·h)]	M <sub>v</sub> × 10 <sup>-4</sup> (g/mol)
325	2	1-adamantyl	~0	
326	3	1-adamantyl	0.28	4.4
327	4	1-adamantyl	0.41	8.6
328	5	1-adamantyl	1.23	3.7
329	6	1-adamantyl	2.64	4.5
330	4	CMe <sub>2</sub> Ph	0.44	2.6
331	6	CMe <sub>2</sub> Ph	9.06	3.8
331 <sup>b</sup>	6	CMe <sub>2</sub> Ph	104	0.9

<sup>a</sup> Polymerization conditions: toluene, 250 mL; complex, 2.0 μmol; MAO, 1.25 mmol; ethylene pressure, 0.1 MPa; 25 °C; 5 min. <sup>b</sup> Complex, 0.08 μmol; 75 °C.

molecular weight products, mainly consisting of methylenecyclopentane derivatives and a small amount of dimers.<sup>224</sup> Salen or salphen Zr complexes afforded only linear chain products under the conditions where (Cp)<sub>2</sub>ZrCl<sub>2</sub>/Et<sub>3</sub>Al/Et<sub>2</sub>Mg produced cyclooligomeric products from ethylene, presumably via a metallacyclic species.<sup>550</sup>

## 6.2. Tetridentate Ligands with Other Metals

The salen and salphen Fe complexes were reported to furnish ethylene oligomerization catalysts when combined with EAO in the high temperature range 90–200 °C, albeit having low to moderate activities.<sup>250,251,498</sup> The V complexes supported by tetridentate Schiff base ligands, where the C<sub>2</sub>-linked bridging moieties were -(CH<sub>2</sub>)<sub>2</sub>- or C<sub>6</sub>H<sub>10</sub>, afforded high molecular weight PEs with large PDI values when activated with Et<sub>n</sub>AlCl<sub>(2-n)</sub>.<sup>169,176,551</sup> The Mn salen complex exhibited little ethylene polymerization activities in homogeneous catalysis. However, when the complex was supported on MgCl<sub>2</sub>, it showed activities in ethylene and propylene polymerization upon activation with Et<sub>2</sub>AlCl. Interestingly, when ethylbenzoate was added to the MgCl<sub>2</sub>-supported catalyst, the obtained PP demonstrated isotacticity (*mmmm* = 80.3%, *T<sub>m</sub>* = 157.5 °C).<sup>248</sup> Redshaw and co-workers synthesized V complexes 335 (Chart 23) bearing flexible thioether bridging groups varied in their length.<sup>239</sup> Upon activation with Me<sub>2</sub>AlCl, the complexes demonstrated high to very high activities (1–11 kg-polymer/(mmol·M·h·bar)) for ethylene polymerization via a single site mechanism, which were comparable to or higher than those of nonbridging V complexes, (L<sup>FI</sup>)<sub>2</sub>VX (X: =O, -Cl). Also, the obtained polymers had higher molecular weights, especially at higher polymerization

Chart 23

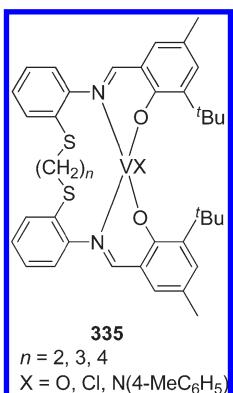
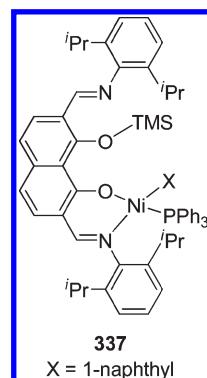


Chart 24



temperatures, while keeping narrower molecular weight distributions, indicating beneficial effects of the sulfur coordination. There were no significant differences observed between the lengths of the thioether bridging groups as regards polymerization characteristics.

Nickel<sup>552</sup> and cobalt<sup>254</sup> salen complexes can polymerize 1,3-butadiene into poly(butadiene)s with high 1,4-cis selectivity (>90%). The Ni complex with  $\text{BF}_3\text{OBu}_2/\text{Et}_3\text{Al}$  furnished an active catalyst ( $\text{Ni}/\text{B}/\text{Al} = 1/12/6$  molar ratio), while with MAO ( $\text{Al}/\text{Ni} = 100$ ), no activity was observed. On the other hand, the Co complexes can be activated by MAO ( $\text{Al}/\text{Co} = 500$ ) and the complexes were more active when  $R^2 = t\text{-Bu}$  than when  $R^2 = \text{Me}$  or  $\text{H}$ .

It was also reported that the (salen)Ni complex can polymerize NBE with MAO<sup>501</sup> or  $\text{B}(\text{C}_6\text{F}_5)_3/\text{MAO}$ .<sup>503</sup> The (salalen)Cr complex 336 (Scheme 11), which had one of the imines reduced to  $\text{CH}_2\text{NRR}'$ , afforded an alternating copolymer of cyclohexene oxide with carbon dioxide in conjunction with onium (ammonium, phosphonium, iminium) salts.<sup>247</sup>

Copolymers of 4-*tert*-butylstyrene (TBS) and 5-ethylidene-2-norbornene (ENB) were obtained with a Ni complex bearing a 1,2-cyclohexylene-bridged Schiff base ligand in conjunction with MAO.<sup>553</sup>

## 7. POLYMERIZATION WITH MULTINUCLEAR PHE-NOXY–IMINE COMPLEXES

There have been many examples of multinuclear (binuclear in most cases) complexes that can be used in olefin polymerization with the expectation that two metal centers may work together in a concerted manner to achieve a higher degree of control over the polymerization reaction, which can be unattainable with mononuclear complexes. However, there are only a few examples that have unambiguously demonstrated the expected binuclear cooperative effects, because it is generally difficult to discern the multinuclear effects from many other potential causes, especially from simple steric effects induced by the other covalently tethered catalytic species as a large (but otherwise innocent in all the other senses) substituent. The introduction of a binuclear scaffold can certainly result in differences in polymerization characteristics in this case, but it will not be considered as binuclear cooperative effects in a true sense. Therefore, appropriate design and synthesis of the corresponding mononuclear complexes as a control and careful side-by-side experiments of those multinuclear and mononuclear complexes are necessary to establish the multinuclear cooperative effects.

Scheme 32

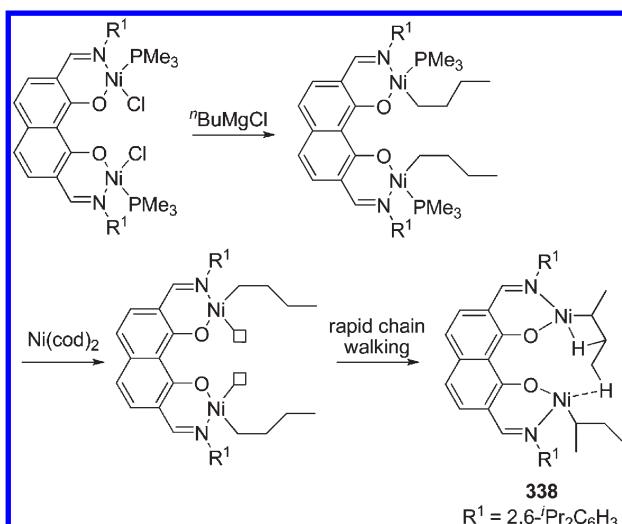
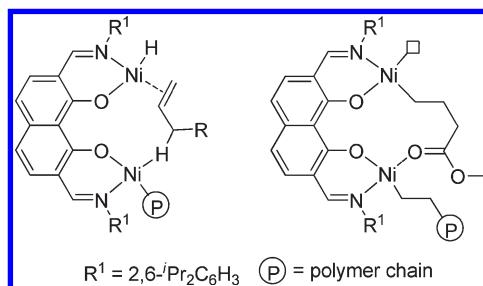


Chart 25



Marks and co-workers synthesized binuclear Ni complexes, where the two metal centers were situated in close proximity within a rigid framework of naphthalene-1,8-diol (complexes 21 and 22 in Scheme 22).<sup>132,134</sup> In comparison with a mononuclear complex 337 (Chart 24), where one OH group was capped with a trimethylsilyl group, the dinuclear complexes were active even without a phosphine scavenger, probably because phosphine dissociation was favored due to crowding bimetallic sites, and exhibited higher activities, higher branch contents, and greater methyl branch selectivities, while the molecular weight and PDI

Chart 26

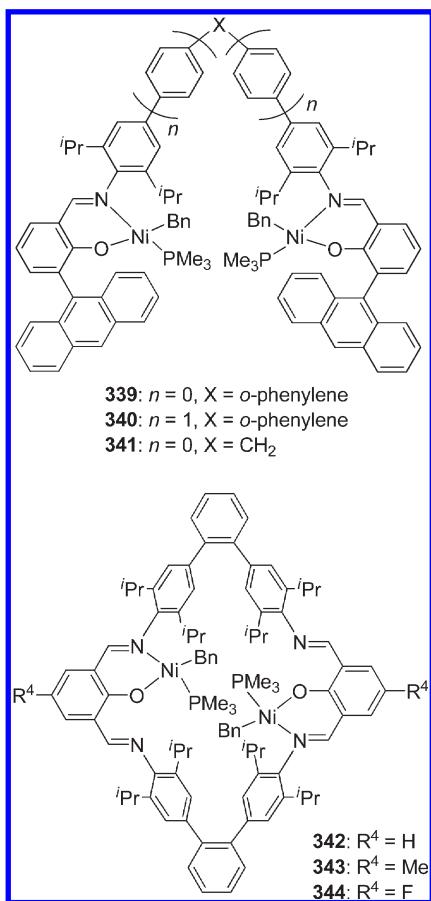
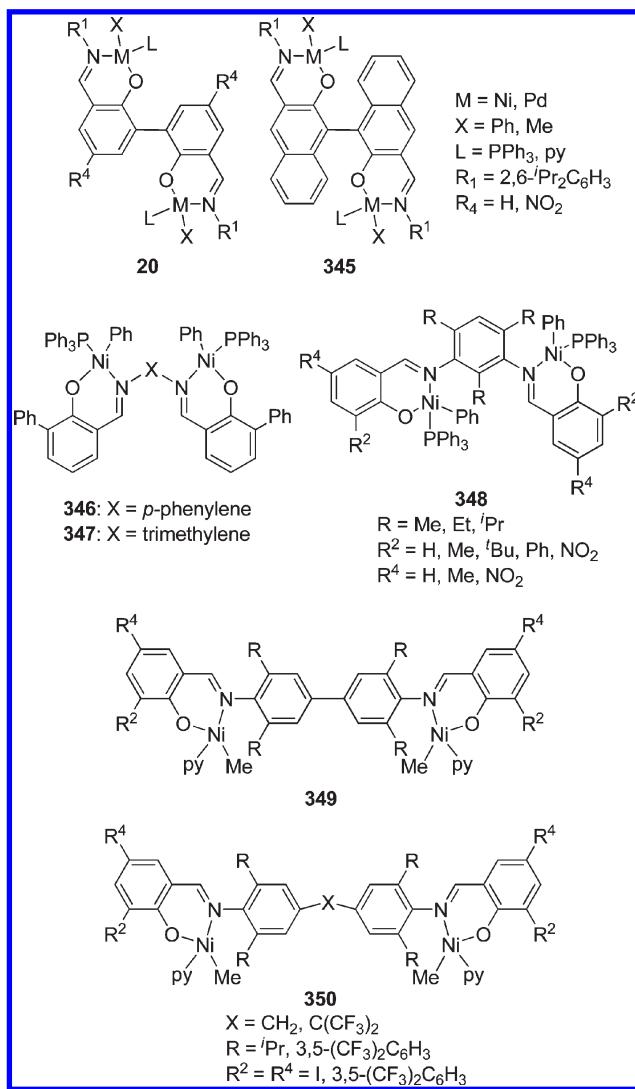


Chart 27



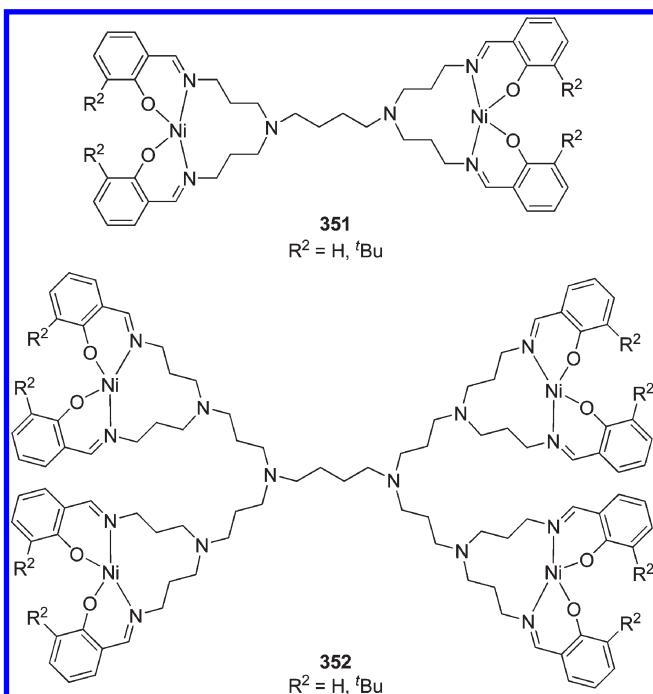
values of the PEs were not significantly different from those obtained with the mononuclear complex. The NMR spectroscopic data of the dibutyl species 338 indicated that intramolecular multiple agostic interactions were at work in a cooperative manner, as shown in Scheme 32. This intramolecular agostic interaction spanning the two proximate metal centers was also suggested to bind substrate monomers (Chart 25), thereby increasing activity and also increasing comonomer incorporation, including polar functional monomers. The group 4 metal complexes having similar ligand motifs were also prepared by the same group. These titanium and zirconium complexes were used in ethylene homo- and copolymerization (comonomer:  $\alpha$ -olefins, styrene, methylenecycloalkanes,  $\alpha,\omega$ -alkadienes) and activated with MAO.<sup>131,133</sup> These complexes showed a similar polymerization behavior to the Ni complexes discussed above; that is, polymerization activities and comonomer incorporation were significantly increased relative to the case of the control mononuclear complexes. Copolymerization of ethylene and methylenecyclohexane with a binuclear Ti complex incorporated up to 11.6% methylenecyclohexane via ring-unopened pathways, while the mononuclear analogue exhibited only 3.4% comonomer incorporation. Interestingly, methylenecyclopentane was incorporated in lesser amounts (<1%) by these complexes, and the Zr analogues gave homo-PE even in the presence of these methylenecycloalkane comonomers.

Lee and co-workers prepared binuclear Ni complexes, which had structurally varied linkers between *N*-aryl groups (339–341; Chart 26).<sup>120</sup> In ethylene homopolymerization, the activities

were comparable to a mononuclear control. The PEs obtained were lower in molecular weights and slightly more branched. In copolymerization with 5-norbornene derivatives ( $2\text{-CH}_2\text{OCOMe}$  and  $2\text{-COOMe}$ ), enhanced activities and comonomer incorporation were observed, for which binuclear monomer binding was proposed in concert with geometry optimized computed structures of the active species. The macrocyclic binuclear complexes 342–344 having a similar backbone were synthesized and characterized by the same group, where the  $\text{Ni}\cdots\text{Ni}$  distance of one of the binuclear complexes was determined to be 8.869 Å.<sup>135</sup> The macrocyclic complexes showed lower activities than the noncyclic binuclear complexes 339 discussed above, possibly due to the low solubility to organic solvents, and therefore, bimetallic effects were not obvious.

Another ligand framework based on biphenyl-2,2'-diol or 1,1'-binaphthyl-2,2'-diol was examined for the synthesis of binuclear Ni and Pd complexes 20 and 345 (Chart 27) by Li and co-workers.<sup>128,129</sup> Each catalytic moiety directly connected ortho to phenoxy (or naphthoxy) oxygens appeared to serve as a bulky  $\text{R}^2$  substituent for the other moiety; consequently, the binuclear complex was active for ethylene polymerization without using a

Chart 28



phosphine scavenger similar to the binuclear complexes by Marks et al., showing activities higher than those of mononuclear complexes in literature data under comparable conditions. These complexes were also active for NBE polymerization. In either case, the obtained PE or poly(NBE) showed slightly larger PDI values (3–4) than the most probable distribution, for which it was suggested that each catalytic moiety served for each other as  $\text{R}^2$  substituents variable in nature as polymerization proceeded.

There have been synthesized and characterized several binuclear Ni complexes having *para*- or *meta*-phenylene  $\text{R}^1$  linkers (346–348).<sup>121–123</sup> Binuclear effects were not particularly discussed for these complexes, although it would be admittedly difficult to expect the property of cooperativity between the two metal centers due to the rigidity of the structures and spatially distant arrangement of the two Ni centers. The binuclear complex 347, having a trimethylene linker ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), was also examined in ethylene polymerization.<sup>121</sup> When activated with MAO, the complex afforded high molecular weight PE with  $\text{PDI} \sim 2$  at 376 g-polymer/(mmol-M·h·bar).

Mecking and co-workers synthesized and characterized a series of binuclear complexes, where two catalytic moieties were connected in the para-position of *N*-aryl groups directly or via  $-\text{CH}_2-$  or  $-\text{C}(\text{CF}_3)_2-$  groups (349 or 350).<sup>75,77</sup> In comparison with the corresponding mononuclear complexes, these binuclear complexes exhibited higher activities and higher polymer molecular weight capabilities in ethylene polymerization at 50 °C polymerization temperature, where the catalysts were the most active. The observed activity enhancement appeared to be attributable to intrinsically high propagation rates for the binuclear complexes rather than to more efficient initiation (dissociation of L), although the reason was not clear.

Mapolie and co-workers applied dendrimer ligand scaffolds to the synthesis of multinuclear Ni phenoxy-imine complexes 351 and 352 (Chart 28).<sup>124</sup> When activated with MAO, the second

Chart 29

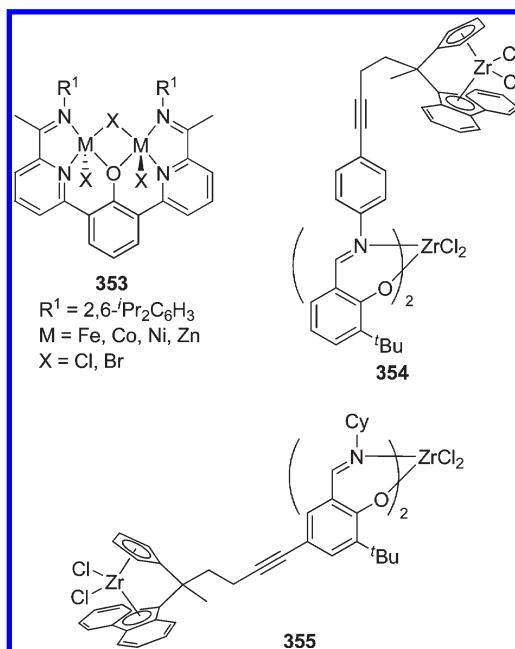
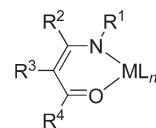


Chart 30



generation catalysts (tetranuclear) showed higher activities in NBE polymerization than the first generation catalysts (binuclear). Binuclear Ni and Pd complexes prepared by Janiak and co-workers also afforded poly(NBE) via a single site polymerization mechanism, whose activities were higher than those of the Ni salen complex.<sup>119</sup>

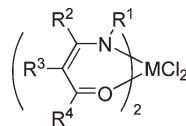
Solan and co-workers synthesized Ni, Fe, Co, and Zn binuclear complexes 353 (Chart 29) supported by a phenoxy-pyridyl-imine ligand.<sup>262</sup> The Ni and Co complexes were active in ethylene oligomerization upon activation with an excess of MAO. A series of trinuclear complexes consisting of two metallocenes and one bis(phenoxy-imine)Zr complex (for example, 354 and 355) were prepared by Alt and co-workers.<sup>266</sup> PEs with rather large PDI values were formed upon activation with MAO, indicating multisited characters of these trinuclear complexes, within which each catalytically active species seemed to work independently.

There were attempts to prepare a macrocyclic binuclear complex using two tetradentate ligands,  $(\text{L}^{\text{FI}-\text{FI}})^{2-}$ , and two group 4 metal precursors, to generate  $(\text{L}^{\text{FI}-\text{FI}})_2(\text{MX}_2)_2$ .<sup>125–127</sup>

## 8. POLYMERIZATION WITH PHENOXY-IMINE RELATED COMPLEXES

### 8.1. $\beta$ -Ketoiminato Complexes

As mentioned in section 1.4,  $\beta$ -ketoiminato,  $(\text{L}^{\text{KI}})^{-}$ , complexes have attracted an increasing amount of attention recently, primarily due to the similarity they hold to the phenoxy-imine ligand; that is, both ligand motifs form a six-membered  $-\text{N}=\text{C}=\text{C}=$

Table 36.  $\beta$ -Ketoiminato Group 4 Metal Complexes for the Olefin Polymerization Catalysts

complex	M	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	ref
356	Zr	'Pr	Me	H	Me	557
	Zr	Ph	Me	H	Me	557
	Zr	4-ClC <sub>6</sub> H <sub>4</sub>	Me	H	Me	557
	Zr	4-(MeO)C <sub>6</sub> H <sub>4</sub>	Me	H	Me	557
	Zr	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	Me	H	Me	233
	Zr	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Me	233
426	Ti	Ph	CF <sub>3</sub>	H	Ph	181–183, 185, 187, 559–563, 565
	Ti	Ph	CF <sub>3</sub>	H	2-C <sub>4</sub> H <sub>3</sub> S	181
	Ti	Ph	CF <sub>3</sub>	H	2-C <sub>4</sub> H <sub>3</sub> O	181
363	Ti	Ph	Me	H	CF <sub>3</sub>	150, 181, 182, 187, 203, 559–563
	Ti	Ph	Me	H	Ph	181
	Ti	4-(MeO)C <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	Ph	183
	Ti	4-MeC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	Ph	183
	Ti	2-MeC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	Ph	183
	Ti	1-naphthyl	CF <sub>3</sub>	H	Ph	183
427	Ti	Ph	CF <sub>3</sub>	H	<sup>t</sup> Bu	182–184, 187, 559–563
	Ti	4-(MeO)C <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	183
	Ti	4-MeC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	183, 184
	Ti	2-MeC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	183
362	Ti	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	150, 203
361	Zr	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	203, 558
357	Ti	2-FC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
360	Ti	3-FC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	4-FC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184, 562
	Ti	2,3-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2,5-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	3,5-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2,3,4-F <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	3,4,5-F <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2-(CF <sub>3</sub> )(C <sub>6</sub> H <sub>4</sub> )	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	3-(CF <sub>3</sub> )(C <sub>6</sub> H <sub>4</sub> )	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	4-(CF <sub>3</sub> )(C <sub>6</sub> H <sub>4</sub> )	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	4-ClC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	4-IC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
364	Ti	4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	Bn	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	Cy	CF <sub>3</sub>	H	<sup>t</sup> Bu	184
	Ti	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	150
	Ti	4-FC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	Ph	562
	Ti	4-FC <sub>6</sub> H <sub>4</sub>	Me	H	CF <sub>3</sub>	562
	Ti	2-FC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub>	H	Ph	185
	Ti	2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	Ph	185
	Ti	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	Ph	185
	Ti	Ph	EtO	H	EtO	186
365	Ti	4-FC <sub>6</sub> H <sub>4</sub>	EtO	H	EtO	186
	Ti	4-MeC <sub>6</sub> H <sub>4</sub>	EtO	H	EtO	186

Table 36. Continued

complex	M	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	ref
358	Zr	Ph	EtO	H	EtO	186
	Zr	4-FC <sub>6</sub> H <sub>4</sub>	EtO	H	EtO	186
	Ti	Ph	<i>n</i> -pentyl	H	CF <sub>3</sub>	187
	Ti	Ph	<i>i</i> Pr	H	CF <sub>3</sub>	187
	Ti	Ph	cyclohexyl	H	CF <sub>3</sub>	187
	Ti	Ph	<sup>t</sup> Bu	H	CF <sub>3</sub>	187
	Ti	Ph	CH=CHPh	H	CF <sub>3</sub>	187
	Ti	Ph	Et	H	CF <sub>3</sub>	187
	Ti	Ph	<i>n</i> -undecyl	H	CF <sub>3</sub>	187
	Ti	Ph	CF <sub>3</sub>	H	<i>n</i> -pentyl	187
	Ti	Ph	CF <sub>3</sub>	H	<i>i</i> Pr	187
	Ti	Ph	CF <sub>3</sub>	H	cyclohexyl	187
	Ti	Ph	CF <sub>3</sub>	H	CH=CHPh	187
	Ti	Ph	CF <sub>3</sub>	H	CHPh <sub>2</sub>	187
	Ti	Ph	CF <sub>3</sub>	H	CF <sub>3</sub>	187
	Zr	Ph	Me	H	CF <sub>3</sub>	558
	Zr	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	558
359	Zr	2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	558
	Ti	Ph	CF <sub>3</sub>	H	3-FC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	4-ClC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2-(Br)C <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	C <sub>6</sub> F <sub>5</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2-FC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	4-FC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	4-(MeO)C <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	3-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2-ClC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2-IC <sub>6</sub> H <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	3,5-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	4-(OMe)C <sub>6</sub> F <sub>4</sub>	565
	Ti	Ph	CF <sub>3</sub>	H	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	565

C—O— chelating structure with a metal center, and they are accessible via a relatively straightforward synthesis, which allows the construction of a large and diverse ligand library. Nevertheless, the steric and electronic characteristics of L<sup>KI</sup> and L<sup>FI</sup> ligand frameworks may be substantially different, apparently seen from the spatial location of their substituents (the numbering of substituents was defined and is shown in Chart 30), the structural rigidity of the chelate ring, and differences in the state and degree of the  $\pi$ -electron conjugation.

As far as we know, the first report on olefin polymerizations catalyzed by a  $\beta$ -ketoimato complex was published in 1988 by Doi and co-workers for propylene polymerization by a vanadium complex, (L<sup>KI</sup>)<sub>3</sub>V(III), although the complex was not particularly better than other tris( $\beta$ -diketonato) vanadium complexes that can mediate living propylene polymerization at a low temperature of below  $-60^{\circ}\text{C}$ . Early work on nickel or cobalt complexes bearing  $\beta$ -ketoimato also appeared as ethylene oligomerization

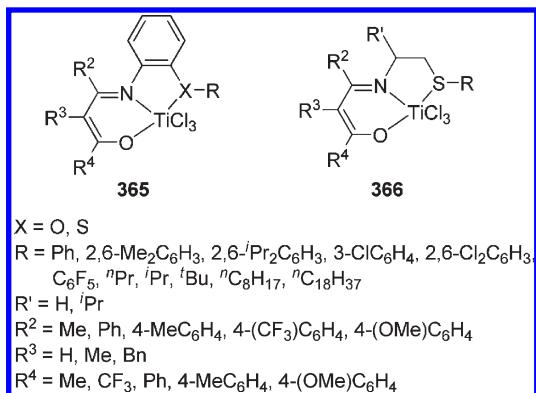
catalysts in 1992.<sup>173,554</sup> Subsequently, Jordan and co-workers prepared zirconium alkyl complexes supported by acen and its derivatives, generated cationic species, and applied them to ethylene polymerization (see section 3.2.1).<sup>179,532</sup> Cavell and co-workers found that highly active ethylene oligomerization catalysts could be generated from a mixture of  $\beta$ -aminoketones, ZrCl<sub>4</sub>, and alkylaluminum chlorides.<sup>555</sup> A detailed study into this revealed that complexes of the type (L<sup>KI</sup>)<sub>2</sub>ZrX<sub>2</sub>, which have *cis*-N/*trans*-O/*cis*-Cl configurational disposition, were likely to be active ethylene oligomerization catalysts or catalyst precursors.<sup>556,557</sup> The activities of complex 356 reached TOF = 54,420 h<sup>-1</sup> (1.5 kg·polymer/(mmol·M<sup>-1</sup>·h) at 3.5 MPa ethylene pressure) upon activation with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>.

Although the pioneering work of Jordan and Cavell described above shows some potential of the  $\beta$ -ketoimato group 4 metal complexes, more extensive research on  $\beta$ -ketoimato complexes, mostly focusing on group 4 metals and Ni, has been carried out after phenoxy-imine group 4 metal and Ni complexes were

revealed to show high performance in olefin polymerization in 1998 (see section 1.2).

**8.1.1.  $\beta$ -Ketoiminato Group 4 Metal Complexes.** Group 4 metal olefin polymerization catalyst precursors having  $\beta$ -ketoimine ligands are summarized in Table 36. These  $(L^{KI})_2MX_2$

Chart 31



complexes ( $M$ : group 4 metals) may have five configurational isomers, as do  $(L^{FI})_2MX_2$  complexes, and Li and co-workers revealed in a series of studies that most of the  $(L^{KI})_2MX_2$  adopted the *cis*-N/*trans*-O/*cis*-X geometry as seen for  $(L^{FI})_2MX_2$  complexes. When complexes 357 and 358 have *trans*-N/*trans*-O/*trans*-X geometry, they were unsurprisingly barely active in ethylene polymerization.<sup>184,187</sup> Also in a similar way to the  $(L^{FI})_2MX_2$  complexes, complex 359, having bulky  $R^1$  substituents ( $2,6\text{-}iPr_2C_6H_3$ ), appeared to prefer a *trans*-N/*cis*-O/*cis*-X geometry.<sup>558</sup>

It seems hard to recognize any clear structure/reactivity relationships from the available data. In general,  $R^1$  substituents other than aryl groups tend to show low activities ( $R^1 = \text{benzyl, cyclohexyl}$ ).<sup>184</sup> The Ti complex having  $R^1 = 4\text{-FC}_6H_4$  and  $R^2 = CF_3$  (360) showed an activity at  $9.6 \text{ kg-polymer}/(\text{mmol-M}\cdot\text{h}\cdot\text{bar})$ ,<sup>184</sup> and the Zr complex with  $R^1 = 2,6\text{-F}_2C_6H_3$  and  $R^4 = CF_3$  (361) demonstrated an activity at  $9.2 \text{ kg-polymer}/(\text{mmol-M}\cdot\text{h}\cdot\text{bar})$ , which are the highest numbers achieved among the Ti and Zr complexes in this category.<sup>558</sup> However, the electronic effects of the  $R^1$  cannot be argued for or against straightforwardly because the degree of electron withdrawing

Table 37.  $\beta$ -Ketoiminato Ni Complexes for the Ethylene Polymerization Catalysts

complex	$R^1$	$R^2$	$R^3$	$R^4$	X	L	ref
373	2,6- $iPr_2C_6H_3$	CF <sub>3</sub>	H	Ph	Ph	PPh <sub>3</sub>	276
	2,6- $iPr_2C_6H_3$	Me	H	Ph	Ph	PPh <sub>3</sub>	276
	2,6- $iPr_2C_6H_3$	Me	H	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	276, 279
	4-(MeO)C <sub>6</sub> H <sub>4</sub>	H	CN	OEt	Mes	PPh <sub>3</sub>	286
	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	CN	OEt	Mes	PPh <sub>3</sub>	286
	2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	CN	OEt	Mes	PPh <sub>3</sub>	286
	4-MeC <sub>6</sub> H <sub>4</sub>	H	COOEt	OEt	Mes	PPh <sub>3</sub>	286
	2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	COOEt	OEt	Mes	PPh <sub>3</sub>	286
367	2,6- $iPr_2C_6H_3$	H	COOEt	OEt	Mes	PPh <sub>3</sub>	286
	2,6- $iPr_2C_6H_3$	H	COOEt	Me	Mes	PPh <sub>3</sub>	286
	2,6- $iPr_2C_6H_3$	H	COOEt	"Pr	Mes	PPh <sub>3</sub>	286
	2,6- $iPr_2C_6H_3$	H	COCF <sub>3</sub>	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	279
	2,6- $iPr_2C_6H_3$	Me	COCF <sub>3</sub>	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	279
	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	COCF <sub>3</sub>	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	279
	2,6-(3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	COCF <sub>3</sub>	CF <sub>3</sub>	Me	PPh <sub>3</sub>	300
	2,6- $iPr_2C_6H_3$	Me	CN	Me	Bn	PM <sub>3</sub>	293
	2,6- $iPr_2C_6H_3$	H	H	Ph	Ph	PPh <sub>3</sub>	277
	2,6- $iPr_2C_6H_3$	H	H	2-biphenyl	Ph	PPh <sub>3</sub>	277
	2,6- $iPr_2C_6H_3$	H	H	9-anthracenyl	Ph	PPh <sub>3</sub>	277
	2,6- $iPr_2C_6H_3$	Me	H	2-biphenyl	Ph	PPh <sub>3</sub>	277
	2,6- $iPr_2C_6H_3$	CF <sub>3</sub>	H	2-biphenyl	Ph	PPh <sub>3</sub>	277
	2,6- $iPr_2C_6H_3$	H	indene		Ph	PPh <sub>3</sub>	278
	2,6- $iPr_2C_6H_3$	H	dihydronaphthalene		Ph	PPh <sub>3</sub>	278
	2,6- $iPr_2C_6H_3$	H	benzoannulene		Ph	PPh <sub>3</sub>	278
	2,6- $iPr_2C_6H_3$	H	indene		Me	py	278
	2,6- $iPr_2C_6H_3$	H	dihydronaphthalene		Me	py	278
	2,6- $iPr_2C_6H_3$	H	benzoannulene		Me	py	278
	2,4,6- $iPr_3C_6H_2$	phenylene	H		<i>o</i> -tolyl	PPh <sub>3</sub>	287

properties of the R<sup>1</sup> substituents was not necessarily in accord with the catalytic efficiencies of the complexes.

Mecking and co-workers demonstrated that a Ti complex 362 bearing 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> as R<sup>1</sup> furnished a living ethylene polymerization catalyst with MAO, affording PE with extremely narrow molecular weight distributions.<sup>150,203</sup> On the other hand, the complexes having R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub> or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (363 and 364) afforded PE with ordinary PDI values. The difference in activation efficiency was suggested for the ortho-substituent effects. Ethylene polymerization with the Ti complex 362 proceeded in a robust living manner up to 75 °C, and a diblock copolymer, PE-*b*-aPP, was also accessible. It is intriguing to remember that similar nonsteric *ortho*-F effects were observed for a series of bis(phenoxy-imine) Ti complexes (see also section 4.1.1.2).

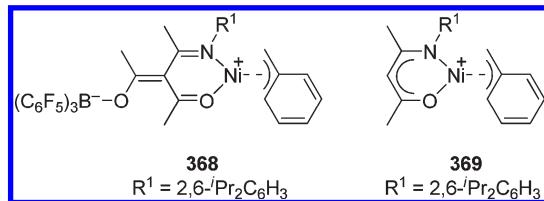
Li and co-workers investigated copolymerization of ethylene with α-olefins,<sup>559,560</sup> NBE,<sup>181,183</sup> cyclopentene,<sup>182</sup> cyclopentadiene,<sup>561</sup> 5-vinyl-2-norbornene or 5-ethylidene-2-norbornene,<sup>562</sup> DCPD,<sup>185,563</sup> and 2,5-norbornadiene<sup>563</sup> using various (L<sup>KI</sup>)<sub>2</sub>TiCl<sub>2</sub> complexes with MMAO. A complex 363 demonstrated higher comonomer uptake in most cases. Under mild conditions, this complex also exhibited quasi-living ethylene polymerization characteristics, which were even more prominent in the copolymerization of ethylene and cyclic olefins. This living nature allowed the preparation of essentially alternating copolymers of ethylene and various cycloolefins with narrow molecular weight distributions and diblock copolymers such as PE-*b*-poly(ethylene-*co*-NBE), PE-*b*-poly(ethylene-*co*-cyclopentene), or PE-*b*-poly(ethylene-*co*-DCPD). This again resembled the polymerization behavior of bis(phenoxy-imine) Ti complexes<sup>168</sup> and also the bis(pyrrolide-imine) Ti complexes.<sup>52,53</sup> Some of the cyclo-diolefin copolymers having unreacted double bonds in the comonomer units were subject to postpolymerization reactions, in the end achieving functionalized polyolefins (see section 10.3.1).<sup>563</sup>

By introducing pendant donors at the R<sup>1</sup> substituents, Sun, Tang, and co-workers synthesized (in a one pot screening method<sup>180</sup>) and characterized a series of group 4 metal complexes ligated by a tridentate ligand, (L<sup>KI</sup>-L)TiCl<sub>3</sub> (365 and 366; Chart 31), and employed these complexes for ethylene polymerization<sup>180</sup> and ethylene copolymerization with α-olefins,<sup>172,180</sup> with cyclic olefins<sup>172</sup> or with alkylaluminum-masked polar functional olefins.<sup>533</sup> Complexes 365 and 366 were revealed to have their ligands wrapped around the Ti center in a meridional fashion. It is not clear how these three chlorine atoms turn to active species upon activation with MMAO. When compared with similar (L<sup>FI</sup>-L)TiCl<sub>3</sub> complexes, the ethylene polymerization activities were comparable (1–2 kg-polymer/(mmol-M·h·bar)) or somewhat lower but tended to show higher comonomer uptakes in copolymerization. Positive comonomer effects on activities and polymer molecular weights were observed in ethylene/1-hexene and in ethylene/NBE copolymerizations.<sup>172,180</sup>

Hybrid complexes of the type, (Cp')(L<sup>KI</sup>)MX<sub>2</sub>, were prepared and tested as an olefin polymerization catalyst.<sup>233,564</sup>

**8.1.2. β-Ketoiminato Complexes with Ni and Other Metals.** Table 37 summarizes Ni based β-ketoiminato complexes used for olefin oligomerization and polymerization. The unique and highest activity was achieved by Brookhart and co-workers, with complex 367 bearing electron withdrawing trifluoromethyl and trifluoroacetyl groups and phosphine scavengers (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Ni(cod)<sub>2</sub>) at 2.8 kg-polymer/(mmol-M·h·bar), which lasted for hours.<sup>279</sup> Many of these Ni complexes in Table 37 possessed carbonyl or nitrile groups in the ligands, with which B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> generated zwitterionic species in some instances.<sup>291–293,566</sup>

Chart 32



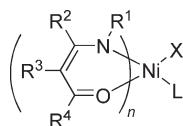
Since the zwitterionic species were more electrophilic at the Ni center, a zwitterionic complex 368 exhibited much higher ethylene polymerization activity (~800 g-polymer/(mmol-M·h·bar)) than the corresponding nonionic complex 369 (~7.5 g-polymer/(mmol-M·h·bar)) (Chart 32).<sup>292</sup>

The β-ketoiminato Ni complexes, such as phenoxy-imine Ni complexes, were very active in NBE polymerization upon activation with MAO, with MMAO, and, in one instance, with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Table 38). Jin and co-workers prepared and characterized the Ni complexes (L<sup>FI</sup>)NiPh(PPh<sub>3</sub>) (252) and (L<sup>KI</sup>)NiPh(PPh<sub>3</sub>) (370, 371) and β-diketoiminato Ni(I) complex 253, and they examined NBE polymerization with MMAO as an activator.<sup>269</sup> All complexes showed rather similar activities at 15–30 kg-polymer/(mmol-M·h). A comparative study between mono- (372, 373) and bis-ligated complexes (374, 375) showed similar activities (45–52 kg-polymer/(mmol-M·h)) despite the number of ligands or the substituents.<sup>275</sup> Li and co-workers also carried out NBE polymerization using a variety of bis-chelated Ni complexes, including β-ketoiminato, β-diketonato, phenoxy-iminato, and pyrrolide-iminato, again revealing similar activities to each other at 6–12 kg-polymer/(mmol-M·h).<sup>326</sup> With B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, (L<sup>KI</sup>)<sub>2</sub>Ni complexes 376 and 377 exhibited similar activities (B/Ni = 5–20), up to 38 kg-polymer/(mmol-M·h).<sup>567</sup> Wu and co-workers demonstrated that (L<sup>KI</sup>)PdMe(PPh<sub>3</sub>) showed much higher activities than (L<sup>KI</sup>)<sub>2</sub>Ni in NBE polymerization.<sup>320</sup>

These Ni complexes can also polymerize MMA upon activation with MAO into syndiotactic-rich poly(MMA),<sup>276,319,321,568</sup> for which a radical pathway initiated by homolytic Ni–C bond fission was proposed by He and Wu,<sup>321</sup> while an insertion mechanism was suggested by Li and co-workers due to a radical quenching experiment by galvinoxyl and the fact that ethylene-rich poly(ethylene-*co*-MMA) was obtained, albeit with extremely large PDI values.<sup>276</sup> Chen and co-workers carried out polymerizations of *n*-butyl methylacrylate (BMA)<sup>569</sup> and styrene<sup>570</sup> using (L<sup>KI</sup>)<sub>2</sub>Ni/MAO and obtained syndiotactic-rich poly(BMA) and atactic polystyrenes, respectively, for which a coordination insertion mechanism was proposed.

Several Pd complexes were prepared and tested in the polymerization of ethylene, NBE, and MMA and copolymerization of NBE and methyl acrylate (MA).<sup>320,334,571–573</sup> For ethylene polymerization, complex 378 (Chart 33) showed up to about 80 kg-polymer/(mmol-M·h·bar) with somewhat large PDI values of 2.4–3.6 with MAO.<sup>334</sup> The same catalysts can polymerize MA into atactic poly(MA) and copolymerize NBE with MA, yielding mixtures separable by solvent fractionation.<sup>571</sup> MMA polymerization with complexes 378 and MAO afforded syndiotactic-rich poly(MMA).<sup>572</sup>

As mentioned at the beginning of this section, a vanadium complex 379 afforded PP at about 30 g-polymer/(mmol-M·h) of activity.<sup>36</sup> More recently, monoligated V(III) complexes, (L<sup>KI</sup>)VCl<sub>2</sub>(thf)<sub>2</sub>, were synthesized, characterized, and examined

Table 38.  $\beta$ -Ketoiminato Ni Complexes for NBE Polymerization

complex	n	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	X	L	ref
374	2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Ph			326
	2	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Ph			322, 326, 575
375	2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>			275, 326
370	1	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Me	Ph	PPh <sub>3</sub>	269
371	1	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Me	Ph	PPh <sub>3</sub>	269
372	2	naphthyl		cyclohexyl		Me		323
	2	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		cyclohexyl		Me		324
	2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		cyclohexyl		Me		324
	2	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		cyclohexyl		Ph		324
	2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		cyclohexyl		Ph		324
	2	naphthyl	Me	H	Me			320, 322
	1	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	275
	1	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	CF <sub>3</sub>	Ph	PPh <sub>3</sub>	275, 575
	2	naphthyl	Me	H	Me			322
	2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Me			322
376	2	Ph	Me	H	Me			322, 567
377	2	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Me			322
	1	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	Ph	Ph	PPh <sub>3</sub>	575
	1	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Me	H	Ph	Ph	PPh <sub>3</sub>	575
	2	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CF <sub>3</sub>	H	Ph			575
377	2	naphthyl	Me	H	Me			506, 567

Chart 33

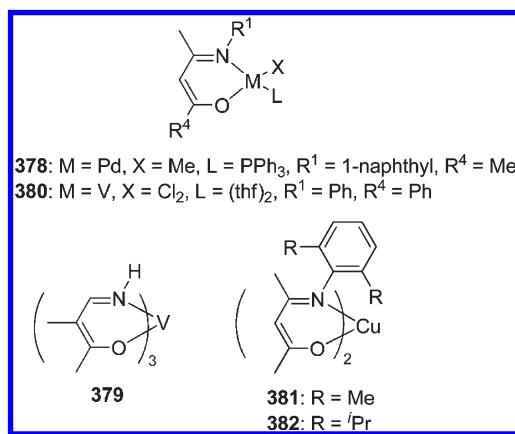
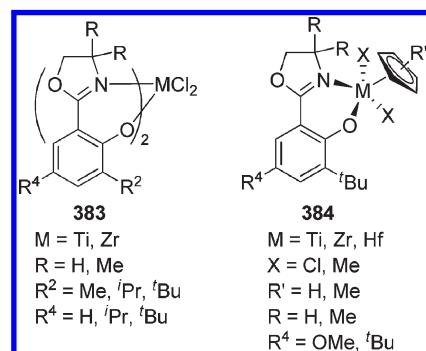


Chart 34



in ethylene polymerization<sup>243,574</sup> and copolymerization with NBE,<sup>243</sup> alkylaluminum-capped  $\alpha$ -olefin- $\omega$ -ols,<sup>518</sup> and  $\alpha$ -olefins<sup>243,574</sup> by Li and co-workers. Upon activation with Et<sub>2</sub>AlCl/ETA, complex 380 exhibited as high as 29 kg-polymer/(mmol·M·h·bar) activity toward ethylene polymerization. In the copolymerization of ethylene and 1-hexene, these complexes showed comparable activities and higher comonomer uptake than VCl<sub>3</sub>(thf)<sub>3</sub>. Bis-ligated V(III) and V(IV) complexes, (L<sup>KI</sup>)<sub>2</sub>VCl(thf) and (L<sup>KI</sup>)<sub>2</sub>VO(thf) were also synthesized, characterized, and tested in ethylene (co)polymerization.<sup>574</sup>

ethylene polymerization activated with Et<sub>2</sub>AlCl/ETA (Al/V = 4000), they showed 8–21 kg-polymer/(mmol·M·h·bar).

Polymerization of MA and copolymerization of MA and 1-hexene were investigated by using a copper complex 381 or 382, although (co)polymerization appeared to proceed in a radical mechanism.<sup>338</sup>

## 8.2. Phenoxy–Oxazoline Complexes

Floriani and co-workers reported in 1995 on the synthesis and characterization of bis(phenoxy–oxazoline) titanium, zirconium, and vanadium complexes.<sup>37</sup> They also reported on the synthesis and characterization of bis(phenoxy–oxazoline) zirconium and hafnium alkyls 1 and 49, the generation of cationic species, and

ethylene polymerization with them (see sections 1.2 and 3.2.1).<sup>38</sup> Following this pioneering work, Bochmann, Scott, and co-workers introduced sterically demanding substituents at the oxazoline ring as well as ortho to the phenoxy oxygen, which have been shown to be extremely beneficial in closely related bis(phenoxy-imine) group 4 metal complexes.<sup>188</sup> Indeed, both Ti and Zr complexes **383** (Chart 34) exhibited higher activities than the Floriani's complexes toward ethylene polymerization when activated with MAO, and the activities were much higher for Zr complexes than Ti congeners. One of the Zr complexes ( $R = Me$ ,  $R^2 = tBu$ ,  $R^4 = H$ ) exhibited an extremely high activity of up to 280 kg-polymer/(mmol-M·h·bar) in a 1 min polymerization. However, the Zr catalysts were thermally unstable and the activity decayed rather rapidly, whereas the Ti catalysts were long-lived. The Ti complexes afforded much higher molecular weight PE than the Zr counterparts, and some of the obtained PE exhibited multimodal molecular weight distributions, possibly due to the presence of structural isomers. These polymerization characteristics bear a strong resemblance to those of bis(phenoxy-imine) group 4 metal complexes. Similar ligand transfer to  $Me_3Al$  to form  $(L^{FO})AlMe_2$  was also observed as a deactivation path.<sup>188,376</sup>

Hybrid complexes of the type  $(C_5R_5)(L^{FO})MX_2$  ( $R: Me, H$ ;  $M: Ti, Zr, Hf$ ;  $X: Cl, Me$ , **384**) were synthesized and characterized by Scott and co-workers.<sup>354</sup> Although the Ti complex showed very low activity and the Hf complex was inactive, the Zr complexes with  $[PhNMe_2H][B(C_6F_5)_4]$  furnished a single site catalyst, which exhibited low to moderate activities in ethylene polymerization. When activated with MAO or  $[Ph_3C][B(C_6F_5)_4]$ , the catalysts showed multisite characteristics. A computational study suggested that these modest activities could be attributed to steric congestion around the metal.

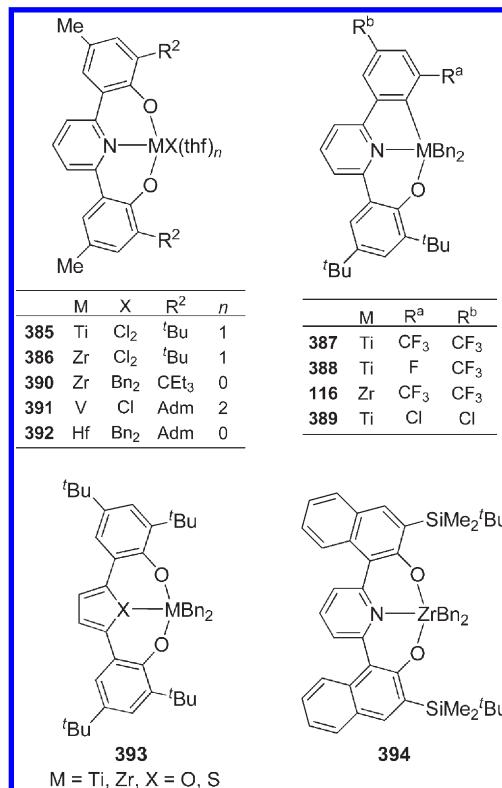
A (phenoxy-oxazoline) Ni complex was found to serve as an ethylene oligomerization ( $C_4-C_8$  olefins, up to 551 g-oligomers/(mmol-M·h) at 1.2 MPa ethylene) and propylene dimerization catalyst when activated with MAO,  $tBu_2AlH$ ,  $Et_3Al$ , and  $Ni(cod)_2$ .<sup>281,282</sup>

### 8.3. Phenoxy-Pyridine Complexes

Fujita and co-workers introduced bis(phenoxy-pyridine) Ti amide complexes (see section 1.2), which upon activation with MAO or  $tBu_3Al/[Ph_3C][B(C_6F_5)_4]$  showed moderate activities up to 564 g-polymer/(mmol-M·h·bar) and afforded high molecular weight polymers.<sup>576</sup> DFT calculations suggest that an active species might have a *trans*-N/*cis*-O/*cis*-(Me, ethylene) configuration.

Chan and co-workers synthesized Ti and Zr complexes **385** and **386** supported by tridentate pyridine-2,6-bis(aryloxide) ligands. The Zr complex **386** exhibited high ethylene polymerization activities up to 5.85 kg-polymer/(mmol-M·h·bar) in combination with MAO, and very high activity at 36.6 kg-polymer/(mmol·h·bar) when activated with  $tBu_3Al/[Ph_3C][B(C_6F_5)_4]$ .<sup>577,578</sup> They also prepared Ti and Zr complexes bearing a pyridine-2-phenolate-6-( $\sigma$ -aryl) [O,N,C] tridentate ligand. Aside from the intramolecular [C—H···F—C] interaction, which was for the first time unequivocally proven for this particular ligand framework in solution and in the solid state (see also section 4.1.2),<sup>447,448</sup> these complexes also served as olefin polymerization catalysts. Upon activation with MAO or  $tBu_3Al/[Ph_3C][B(C_6F_5)_4]$ , Ti complexes **387** and **388**, bearing fluorinated ligands, demonstrated high ethylene polymerization activities (1.8–4.5 kg-polymer/(mmol-M·h·bar)), while a Zr

Chart 35



congener **116** showed somewhat lower activity (<1 kg-polymer/(mmol-M·h·bar)). In copolymerization with propylene or NBE, decent comonomer incorporations were observed. The complexes having Cl, Br, or Me groups instead of F or CF<sub>3</sub> furnished less active catalysts, and Hf complexes were virtually inactive under the conditions examined.<sup>579</sup> At elevated temperatures (for example, 100 °C), a non-fluorinated Ti complex **389** exhibited an activity at 12 kg-polymer/(mmol-M·h) (at 0.7 MPa ethylene) in ethylene polymerization,<sup>580</sup> for which was suggested the possibility of monomer insertion into the Ti—C(aryl) bond to alleviate steric repulsion between the pyridyl 3-H and the substituent at the 5-position of the  $\sigma$ -aryl group in a similar way to a related Hf complex.<sup>581</sup>

Bercaw and co-workers synthesized Ti and Zr complexes bearing a [O,L,O] tridentate ligand (L: pyridine, furan, thiophene) (**390**–**393**). The Ti complexes adopted C<sub>2</sub>-symmetry, while the Zr complexes had C<sub>s</sub>- and C<sub>1</sub>-symmetry. Therefore, propylene polymerization was investigated with relationships between symmetry and stereospecificity in mind.<sup>582,583</sup> A Zr complex **390** having pyridine as a linker L donor exhibited 1.5 kg-polymer/(mmol-M·h) with MAO. The other Zr complexes bearing furan and thiophene linkers also demonstrated high activities. The obtained PP consisted of two discrete components: one had a molecular weight of around 10<sup>5</sup>, and the other component had oligomers having molecular weights of  $M_w \sim 10^3$  g/mol. The Ti counterparts demonstrated much lower activities ( $\times 10^{-3}$ ) for propylene polymerization but afforded a mixture of higher molecular weight polymers, which possessed *mmmm* isotactic sequences in a significant quantity and low molecular weight atactic polymers. Apparently from the X-ray solid state structures, the Ti complexes were more crowded around the

metal than the Zr congeners, which would cause this drastic retardation in activity. Meanwhile, a Ti complex having benzene as a linker instead of pyridine afforded solely low molecular weight atactic polymers. It was thus assumed that the complex with the pyridine linker can generate  $C_2$  symmetric and  $C_s$  symmetric cationic species, each of which produced iso- and atactic polypropylene, respectively. Coordination of aluminum on the pyridyl nitrogen might cause the  $C_s$  symmetric species, which resembled the species from the benzene linker. The vanadium complex with the pyridyl linker (391) exhibited a moderate activity and decent 1-octene incorporation in ethylene/1-octene copolymerization, but the Hf complex 392 only showed a very low activity.

Kirillov, Carpentier, and co-workers prepared similar group 4 metal complexes 394 (Chart 35) supported by pyridine-2,6-bis(naphthoxide), also aspiring for stereospecific polymerization.<sup>584</sup> Although these complexes showed little activities in propylene polymerization, probably due to steric crowdedness imposed by bulky silyl groups, interconversion between  $C_2$  symmetric and  $C_s$  symmetric isomers was proved experimentally and theoretically toward possible formation of stereoblock sequences.

#### 8.4. Other [N,O] Chelate Complexes

Erker and co-workers successfully synthesized a single enantiomer of planarly chiral ferrocene–salimine ligands (*p*-S isomer), which were used to prepare a series of group 4 metal complexes 395 and 396 (Scheme 33).<sup>142,143</sup> In the solid state structures, the octahedral complexes adopt an *trans*-N/*cis*-O/

*cis*-Cl geometry and the Zr and Hf complexes were preferentially crystallized into the  $\Lambda$  diastereomers. However, in solution they exhibited fluxional behavior, possibly with their respective  $\Delta$  diastereomers. For the Ti complexes, the interconversion between  $\Lambda$  and  $\Delta$  diastereomers appeared to be more facile in solution, and both isomers were found in the crystal. Upon activation with MAO, a Ti complex 395 afforded high molecular weight PE at 11 g-polymer/(mmol-M·h·bar) and a Zr complex 396 showed up to 123 g-polymer/(mmol-M·h·bar) activity at 125 °C.

Several Ni or Cu complexes supported by phenoxy-imidazole or phenoxy-thiazole ligands were prepared and used for polymerization of ethylene<sup>385,329,585</sup> and NBE.<sup>328</sup> The phenoxy-imidazole Ni complex showed far higher activity (229 kg-polymer/(mmol-M·h)) than the phenoxy-imidazole Cu complex (316 g-polymer/(mmol-M·h)) for NBE polymerization. The results of ethylene oligomerization or polymerization with phenoxy-imidazole (397–402) or phenoxy-thiazole (403–409) complexes are compiled in Tables 39 and 40.

As another related ligand motif,  $\beta$ -ketoimine ligands having fused pyrazole were complexed with Ni, Cu, Co, and Ti (Table 41) and examined for olefin polymerization.

A significant number of complexes bearing anilinotropone-based ligands were examined, of which the motive was primarily to investigate the five-membered chelate rings instead of the six-membered ones. Since these anilinotropone-based complexes were out of the scope of this review, we herein provide only their structures in Table 42 along with their bibliographic details.

#### 9. HETEROGENIZATION OF PHENOXY-IMINE COMPLEXES

Ziegler–Natta catalysts are heterogeneous solid catalysts in their original form, and also in their most advanced form, they are currently being used on an industrial scale for olefin polymerization. Consequently, slurry and gas-phase processes have been developed for the production of polyolefins (HDPE, LLDPE, iPP, etc.) using these heterogeneous catalysts. The typical challenges in developing an efficient and practical heterogeneous olefin polymerization catalyst are (1) to control the morphology

Scheme 33

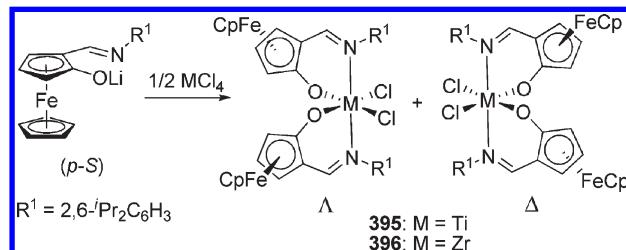
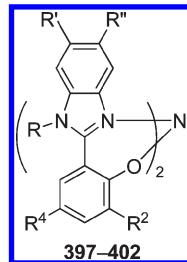
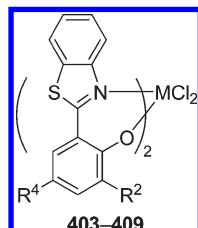


Table 39. Ethylene Oligomerization for the Phenoxy-Benzimidazole Ni Complex<sup>a</sup>



complex	R <sup>2</sup>	R <sup>4</sup>	R	R'	R''	activity [g-oligomer/(mmol-M·h)]
397	H	H	H	H	H	301
398	H	H	H	Me	H	228
399	H	H	H	Me	Me	200
400	H	H	'Pr	H	H	237
401	Cl	Cl	'Pr	H	H	251
402	H	OMe	'Pr	H	H	339

<sup>a</sup> Oligomerization conditions: toluene, 30 mL; Et<sub>2</sub>AlCl, 1.0 mmol; Al/Ni = 200; 20 °C; 30 min; ambient ethylene pressure.

Table 40. Ethylene Polymerization for the Phenoxy–Thiazole Ti and Zr Complexes<sup>a</sup>

complex	M	R <sup>2</sup>	R <sup>4</sup>	activity [g-polymer/(mmol-M·h)]
403	Ti	Me	H	<20
404	Ti	<sup>t</sup> Bu	Me	trace
405	Zr	H	H	40
406	Zr	Me	H	22–106
407	Zr	<sup>t</sup> Bu	Me	522
408	Zr	Cl	H	80
409	Zr	H	Cl	trace

<sup>a</sup> Polymerization conditions: toluene, 50 mL; MAO, 3.0–5.0 mmol; Al/M = 300–500; ethylene pressure, 0.1 MPa; 20–30 °C; 30 min.

of the catalyst and thereby the morphology of the obtained polymer, which results in efficient polymer flow in the process; (2) to achieve high bulk density of the polymers (defined as the mass of polymer particles divided by the total volume they occupy); and (3) to avoid the reactor fouling for stable plant operation for the long-term.

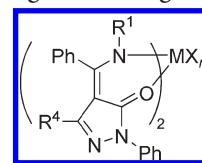
In order for metallocenes and post-metallocenes that are soluble in organic solvents to be applied to slurry or gas-phase processes, these molecular catalysts or their precursors must be anchored onto the surface of the solid supports.<sup>595,596</sup> The additional challenge associated with these solid supported molecular catalysts is how to maintain the virtues of homogeneous molecular catalysts, which are sometimes deteriorated by the heterogenization processes, resulting in lowered activity/selectivity and loss of chemical uniformity (nonstatistical distribution of molecular weight and/or comonomer composition).

In this section, heterogenization of phenoxy–imine based catalysts will be discussed with respect to the solid support employed, among which SiO<sub>2</sub> and MgCl<sub>2</sub> are representative.

### 9.1. SiO<sub>2</sub>-Supported Catalysts

Silica, which was probably most widely employed as a solid support for metallocene-based catalysts, has been used less frequently for phenoxy–imine based catalysts. Repo and co-workers prepared SiO<sub>2</sub>-supported catalysts by heating a toluene solution of (salen)ZrCl<sub>2</sub>(thf) in the presence of SiO<sub>2</sub> and applied them to ethylene polymerization using MAO as a cocatalyst. Interestingly, those SiO<sub>2</sub>-supported catalysts exhibited activities up to >3 kg-polymer/(mmol-M·h) (at 0.5 MPa ethylene pressure), while the homogeneous nonsupported complex only showed 130 g-polymer/(mmol-M·h) (at 0.5 MPa ethylene pressure) under comparable conditions, although no information on the polymer morphology was available.<sup>361</sup>

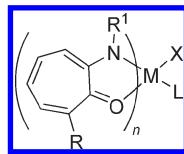
Yu and co-workers used a different protocol; that is, dried SiO<sub>2</sub> was treated with MMAO in excess to surface Si—OH groups, and then with the complex **296** (Ar = Ph) (see section 5.1).<sup>113</sup> Each step was followed by washing with solvent.<sup>597</sup> The supported catalysts showed lower activities than homogeneous nonsupported catalysts, and the resulting polymers had large molecular

Table 41. List of the Ni, Co, Cu, and Ti Complexes Supported by the  $\beta$ -Ketoimine Ligands Having Fused Pyrazole

complex	M	R <sup>1</sup>	R <sup>4</sup>	n	X	ref
428	Ni	4-FC <sub>6</sub> H <sub>4</sub>	Me	0		258
	Co	4-FC <sub>6</sub> H <sub>4</sub>				258
	Ni	Ph				325, 327, 586, 587
		Bn				586, 587
		2-MeC <sub>6</sub> H <sub>4</sub>				325, 586, 587
		naphthyl				325, 327, 586–588
		2-ClC <sub>6</sub> H <sub>4</sub>				327
		4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>				325, 586, 587
	Cu	BnM				589
		Ph				589
Ti		2-MeC <sub>6</sub> H <sub>4</sub>				589, 590
		naphthyl				589
		4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>				589
		Ph	Ph	2	Cl	591
		2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>				
		Bn				
		(CH <sub>2</sub> ) <sub>2</sub> Ph				

weight distributions and higher melting temperatures and also claimed to have larger molecular weights and somewhat improved morphology. In a similar approach, Carlini and co-workers prepared heterogeneous SiO<sub>2</sub>/MAO/(L<sup>FI</sup>)<sub>2</sub>Ni complex **410** catalysts with varying Al/Ni molar ratios (Chart 36).<sup>384</sup> The supported catalysts showed improved activities (up to 550 g-polymer/(mmol-M·h) at 5 MPa ethylene pressure) compared to those of a homogeneous one (160 g-polymer/(mmol-M·h) also at 5 MPa ethylene pressure). However, the obtained PE exhibited large PDI values. Their attempts to transform an ethylene oligomerization catalyst into an ethylene polymerization catalyst

Table 42. List of the Anilinotropone-Based Ni, Al, and Ti Complexes for the Ethylene and Hexene Polymerization Catalysts



M	n	X	L	R <sup>1</sup>	R	monomer	ref
Ni	1	Ph	PPh <sub>3</sub>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene, hexene	592, 593 395, 594
Ni	1	Ph	PPh <sub>3</sub>	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2- <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2-Me-6- <sup>t</sup> BuC <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2,6-Ph <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2,6-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	C <sub>6</sub> F <sub>5</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2-MeC <sub>6</sub> H <sub>4</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2-Me-6-(CF <sub>3</sub> )C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	593
Ni	1	Ph	PPh <sub>3</sub>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Ph	ethylene	404, 593
Ni	1	Ph	PPh <sub>3</sub>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1-naphthyl	ethylene	404, 593
Ni	1	Ph	PPh <sub>3</sub>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-(MeO)C <sub>6</sub> H <sub>4</sub>	ethylene	404
Ni	1	Ph	PPh <sub>3</sub>	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	ethylene	404
Ni	1	Et	2,4-lutidine	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	404
Ni	1	Me	pyridine	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	78
Al	1	Me <sub>2</sub>		2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H		342
Al	1	Me <sub>2</sub>		C <sub>6</sub> F <sub>5</sub>	H		342
Al	2	Me		2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H		342
Ti	2	Cl <sub>2</sub>		C <sub>6</sub> F <sub>5</sub>	H	ethylene	353
Ti	2	Cl <sub>2</sub>		2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	ethylene	353
Ti	1	CpCl <sub>2</sub>		C <sub>6</sub> F <sub>5</sub>	H	ethylene	353

by heterogenization on SiO<sub>2</sub>/MAO failed, and neither activity or selectivity was improved.<sup>80</sup>

Li and co-workers prepared phenoxy-imine Ni complexes that possessed a free hydroxyl group in the ligands ((HO-L<sup>FI</sup>)NiR(L), **224**; see section 4.2.1). These complexes were reacted with Me<sub>3</sub>Al-treated SiO<sub>2</sub>, presumably resulting in a covalent Si—O—Al—(O—L<sup>FI</sup>)NiR(L) linkage on the surface. The supported catalysts showed lower activities than the homogeneous catalysts, but the obtained PE with the supported catalysts possessed higher molecular weights, somewhat large PDI values (2.7–5.0), and higher melting temperatures (lower branch density).<sup>273</sup> Mecking and co-workers made another attempt for covalent anchoring using bis(phenoxy-imine)Ti complexes.<sup>202</sup> Silica nanoparticles ( $D_{av} \sim 50$  nm) were modified by (*n*-octyl)Si(OMe)<sub>3</sub> to make a stable dispersion in organic solvents such as toluene, and the remaining Si—OH groups on the modified silica and phenoxy-imine Ti complexes that have a —O(CH<sub>2</sub>)<sub>3</sub>Si(OMe)<sub>3</sub> linker (**411** and **412**) were covalently attached through condensation. The obtained supported catalysts demonstrated the polymerization characteristics of a single-site catalyst and afforded UHMWPE, during which fragmentation of the catalyst particles into ~8 nm subparticles was observed.

## 9.2. MgCl<sub>2</sub>-Supported Catalysts

Since the late 1960s, MgCl<sub>2</sub> has been employed as a support of the Ti-based Ziegler–Natta catalysts. The most advanced heterogeneous MgCl<sub>2</sub>-supported Ti catalysts have reached an astoundingly high performance level in terms of activity, stereoselectivity for propylene polymerization, and control of the polymer morphology, and they are still the most widely used catalysts in the polyolefin industry.<sup>5,598,599</sup> During this modern period, a wide variety of technologies have been developed to prepare a MgCl<sub>2</sub> catalyst support with a large specific surface area and controlled morphology, despite the fact that, under normal conditions, MgCl<sub>2</sub> is a highly crystalline solid with very low surface area. It should be noted that MgCl<sub>2</sub> was also found to significantly enhance the rate constant of olefin insertion reactions, thus serving as an activator as well as a catalyst support.

Knowing the dual roles (activator and support) of MgCl<sub>2</sub> in olefin polymerization catalysis as the inventor and the manufacturer of MgCl<sub>2</sub>-supported Ti catalysts,<sup>600,601</sup> Fujita and co-workers at Mitsui Chemicals applied MgCl<sub>2</sub> to bis(phenoxy-imine) catalyzed polymerization in the hope that these complexes bearing heteroatom donors would have far stronger affinity to the Lewis acidic surface of MgCl<sub>2</sub> than Cp-based metallocene complexes, with which MgCl<sub>2</sub>-supported catalysts promoted olefin polymerization, albeit at a rather low

Chart 36

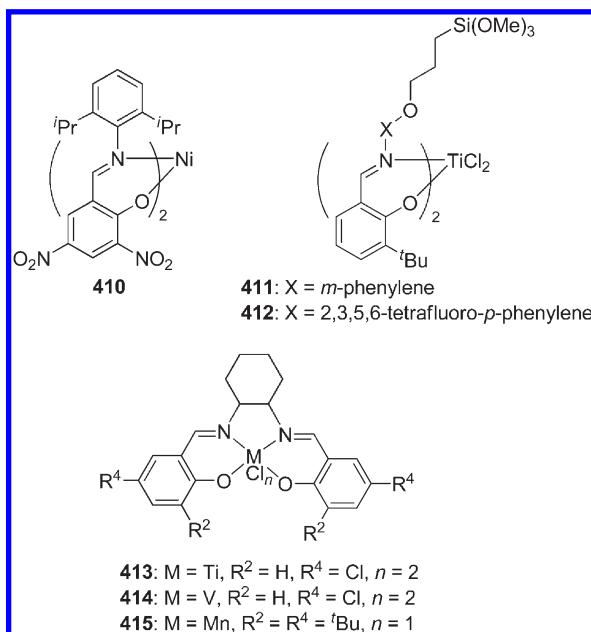
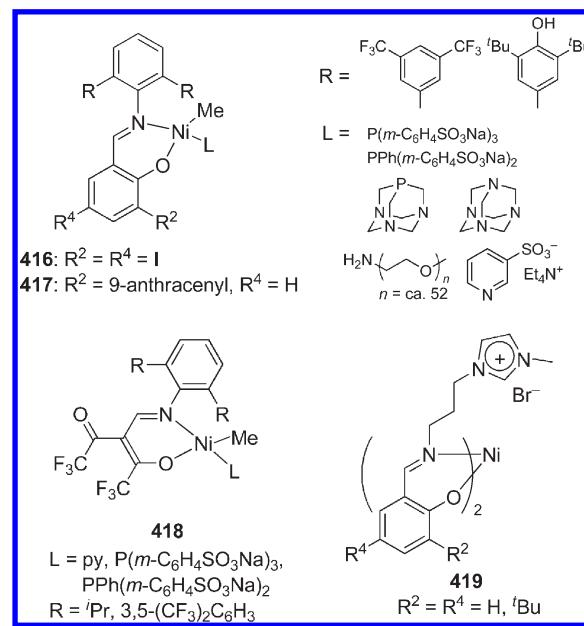


Chart 37



rate.<sup>602–606</sup> First of all, MgCl<sub>2</sub> was dissolved in *n*-decane as the adducts with 2-ethyl-1-hexanol (EHA) (EHA/Mg = 6:1 mol/mol). Subsequent dealcoholysis of the MgCl<sub>2</sub>·(EHA)<sub>n</sub> adducts with *t*Bu<sub>3</sub>Al yielded the solid support consisting of MgCl<sub>2</sub>/*t*Bu<sub>n</sub>Al(OR)<sub>n</sub>, whose size of MgCl<sub>2</sub> crystallites is 28 Å on average.<sup>517,607–609</sup> The obtained solid did work as catalyst support as well as activator without adding any other cocatalysts such as MAO or perfluoroaryl boranes or borate salts. The ethylene polymerization activities of bis(phenoxy-imine) Ti catalysts supported on the MgCl<sub>2</sub>/*R'*<sub>n</sub>Al(OR)<sub>n</sub> (*R'*: *t*Bu, Et) were very high and roughly comparable with those activated with MAO, and the polymer properties (molecular weight, molecular weight distribution, stereoselectivity, livingness, comonomer composition and distribution, etc.) were also similar to each other, which means that the single site characteristics and reaction mechanisms are maintained on the MgCl<sub>2</sub>/*R'*<sub>n</sub>Al(OR)<sub>n</sub> supported catalysts (single site heterogeneous catalysts).<sup>373,517,607–610</sup> This MgCl<sub>2</sub>/*R'*<sub>n</sub>Al(OR)<sub>n</sub> catalyst support was also effective for bis(phenoxy-imine) Zr catalysts, reaching an extremely high activity of 1820 kg-polymer/(mmol-M·h) at 0.9 MPa ethylene pressure.<sup>516</sup> Combination of phenoxy-imine V catalysts with the MgCl<sub>2</sub>/*R'*<sub>n</sub>Al(OR)<sub>n</sub> catalyst support furnished highly active supported V catalysts at elevated temperatures with a longer operating catalyst life, which is outstanding when compared with the case of homogeneous VOCl<sub>3</sub>/Et<sub>2</sub>AlCl/ETA catalyst systems (see section 4.3.2). Under the carefully controlled conditions (alkylaluminums, alcohols for MgCl<sub>2</sub> adduct formation, addition rates of alkylaluminums, temperature profiles for the particle formation, etc.), the MgCl<sub>2</sub>/*R'*<sub>n</sub>Al(OR)<sub>n</sub> catalyst supports can be prepared into nearly perfectly spherical particles free from agglomerations having a wide range of controllable particle sizes (1–15 μm) and narrow size distributions, which are replicated through polymerization in the spherical noncoherent polymer particles with varied sizes, narrow size distributions, and high bulk densities.<sup>609</sup>

Chadwick and co-workers used a spherical MgCl<sub>2</sub>/EtOH adduct as a starting material, which is subject to dealcoholysis

by various alkylaluminums (Me<sub>3</sub>Al, Et<sub>2</sub>Al, *t*Bu<sub>3</sub>Al, (*n*-octyl)<sub>3</sub>Al, Et<sub>2</sub>AlCl) to afford a similar MgCl<sub>2</sub>-based catalyst support (MgCl<sub>2</sub>/AlR<sub>n</sub>(OEt)<sub>3-n</sub>) (for example, refs<sup>611–613</sup>). The MgCl<sub>2</sub>/AlR<sub>n</sub>(OEt)<sub>3-n</sub> supports were revealed to serve as an efficient activator in the absence of MAO or perfluoroaryl boron-based cocatalysts, especially for a bis(phenoxy-imine) Ti catalyst and several mono-Cp Ti catalysts.<sup>614,615</sup> Similar approaches were examined by others. Sun and co-workers used an MgCl<sub>2</sub>/EtOH adduct and MAO for dealcoholization. The obtained catalyst supports were examined with Ni complexes for NBE polymerization. The supported Ni catalysts exhibited in general somewhat lower activities and slightly larger PDI values but were capable of affording higher molecular weight spherical polymers.<sup>387,616</sup> There were no apparent differences between MgCl<sub>2</sub>- and SiO<sub>2</sub>-supported catalysts. Mao and co-workers also employed an MgCl<sub>2</sub>/EtOH adduct, which was dealcoholized thermally and subsequently by MAO. With a bis(phenoxy-imine) Zr complex (63: R<sup>1</sup> = cyclohexyl, R<sup>2</sup> = *t*Bu), an MgCl<sub>2</sub>/MAO support furnished PE particles with 0.36 g/mL of bulk density with the efficiency of up to 29 kg-polymer/(mmol-M·h) at 1.0 MPa ethylene (*M*<sub>w</sub> = 2.5 × 10<sup>4</sup>, PDI = 3.29).<sup>617</sup> Bialek and co-workers similarly employed an MgCl<sub>2</sub>/EtOH adduct and dealcoholized with Et<sub>3</sub>Al or Et<sub>2</sub>AlCl to obtain the MgCl<sub>2</sub>-based catalyst supports. When Et<sub>2</sub>AlCl was used for dealcoholysis, higher activities were achieved (the order of 10<sup>3</sup> g-polymer/(mmol-M·h)) than when Et<sub>3</sub>Al was used with Ti complex 413, but the molecular weight distributions of the obtained PE were somewhat broad. These MgCl<sub>2</sub> catalyst supports exhibited much higher activities than SiO<sub>2</sub>-based catalyst supports.<sup>618</sup> They also used MgCl<sub>2</sub>(thf)<sub>2</sub> as a starting material with a V salen complex 414, which afforded moderately active ethylene polymerization catalysts (up to 4.8 kg-polymer/(mmol-M·h) at 0.5 MPa ethylene) with bulk densities at 0.11–0.23 g/mL. However, the molecular weight distributions of the PEs were very broad (PDI > 10), showing that they were not single site catalysts.<sup>619</sup> Ban and co-workers demonstrated that the MgCl<sub>2</sub>-supported Mn complex 415 exhibited ethylene and propylene polymerization

activities, albeit at low to very low efficiency, but significantly higher than those of the polymerization without  $MgCl_2$ . Also suggested was the possibility of reductive elimination of the ligands of the Mn complexes. With aromatic ester compounds, the Mn catalysts showed high isospecificity up to  $mmmm = 94.0\%$  in propylene polymerization in a similar manner to the  $MgCl_2$ -supported  $TiCl_4$  catalysts.<sup>248</sup>

### 9.3. Emulsion Polymerization

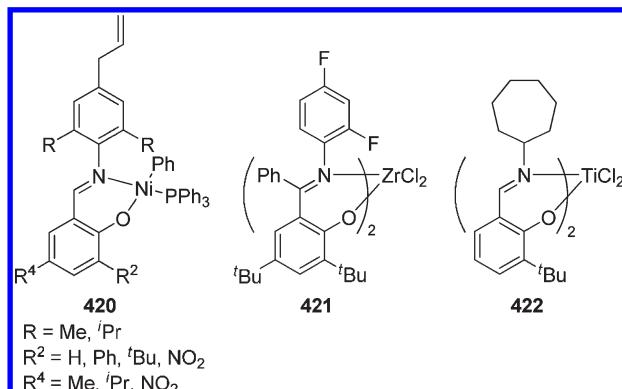
Due to their low oxophilicity, late transition metal complexes are much more tolerant to polar additives than early metal complexes. This nature prompted researchers to investigate late metal catalyzed olefin polymerization in protic media, particularly in water, which may be able to directly produce polyolefin latexes through an environmentally benign process that requires few organic solvents.<sup>66,620–624</sup>

Mecking and co-workers found that PE or poly(ethylene-*co*-NBE) could be produced in water using neutral ( $L^{FI}$ )Ni complexes. The activities of these polymerizations were lower than those in organic solvents, primarily due to the low concentration of ethylene in aqueous media, but water did not show an apparent influence on polymerization characteristics and the catalysts were active for several hours. From  $[P,O]$  chelated water-soluble Ni complexes, low molecular weight PE latexes were generated in the presence of surfactants.<sup>67</sup> By using surfactants and ultrasound or homogenizer, a phenoxy-imine Ni complex **209** in a small amount of toluene can be finely dispersed ( $\sim 100$  nm) in water. By applying ethylene monomer to this emulsion, high molecular weight semicrystalline PE latexes (particle size: 90–350 nm) were successfully obtained.<sup>68</sup> Copolymerization of ethylene with 1-butene or NBE<sup>72</sup> and homopolymerization of  $\alpha$ -olefins (propylene, 1-butene, 1-hexene)<sup>73</sup> were also investigated in aqueous emulsion. Theoretical study suggested that these Ni complexes preferentially bound ethylene over water, although hydrolysis of Ni–R bonds is a possible deactivation path.<sup>625</sup>

As discussed in section 3.2.2, ( $L^{FI}$ )NiMe( $L$ ) complexes **416** and **417** (Chart 37) can be made water-soluble by using hydrophilic or amphiphilic  $L$  ligands. These water-soluble Ni complexes were more active in water than in toluene under certain conditions, presumably due to slow recombination of  $L$  that was dissociated away into water, leaving the Ni species in lipophilic polymer particles.<sup>70,74</sup> In the presence of surfactant and in the absence of any organic solvents, these Ni complexes generated very fine PE particles (4–6 nm), for which each particle was estimated to consist of roughly one PE molecule. From these observations, it was suggested that the particle size of polymers could be correlated to the degree of catalyst dispersion before a polymerization reaction. Aqueous emulsion polymerization was studied also by using binuclear phenoxy-imine Ni complexes **349** and **350**<sup>75</sup> and enolatoimine Ni complexes **418**,<sup>300,301</sup> and also using CuX (X: Cl, Br, I) as a phosphine scavenger.<sup>268</sup>

Lipophilic molecules can be taken up in the PE nanoparticles prepared by aqueous emulsion polymerization catalyzed by the Ni complexes discussed above. Since these molecules preferentially exist in amorphous parts in the PE particles, they experience a different degree of polarity around them depending on the crystallinity of the particles; that is, the more crystalline the polymer particles become, the more polar environments the probe molecule experiences because the molecule tends to exist in amorphous parts at the interfacial periphery of the particles.<sup>303</sup>

Chart 38



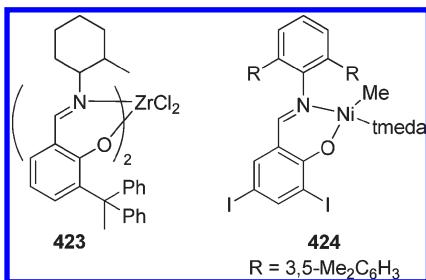
Mecking and co-workers also studied ethylene polymerization and ethylene/NBE copolymerization in supercritical carbon dioxide (scCO<sub>2</sub>) as a reaction medium.<sup>76–78</sup> By introducing a number of fluorine containing groups, Ni complexes can be made soluble in scCO<sub>2</sub>. These complexes served as a single component catalyst for ethylene polymerization in scCO<sub>2</sub>, whose activities were only slightly lower than those in toluene, indicating that CO<sub>2</sub> did not significantly compete with ethylene for binding at the Ni center. The activities decreased in CO<sub>2</sub> of lower density, probably because of decreased solubility of the Ni complexes. Polymerization at 30 °C exhibited a living character (PDI = 1.3). At higher temperature, the activities became higher and more branched polymers were formed, but at 70 °C, the polymer molecular weights dropped significantly, for which it was suggested that CO<sub>2</sub> may help chain transfer in an associative manner. Under appropriate conditions, practically linear (<1 branches/1000C) high molecular weight PE could be obtained.<sup>78</sup>

Wu and co-workers prepared bis(phenoxy-imine) Ni complexes bearing a 1-methylimidazolium bromide moiety as the R<sup>1</sup> substituent (**419**) and applied them to ethylene oligomerization in a biphasic system of an ionic liquid (IL) and organic solvents (toluene or heptane).<sup>315</sup> Interestingly, much higher activities were observed in the biphasic systems than those in organic solvents. Since the majority of the Ni complexes existed in the IL phase, the catalysts were proved to be recyclable by decanting the organic phase and adding solvent, Et<sub>2</sub>AlCl, and ethylene monomer again.

### 9.4. Other Heterogenization Methods

A self-immobilization approach has been examined in metallocene catalyzed polymerization, where the metallocene complexes bearing olefinic portions in their ancillary ligands are expected to be copolymerized during the polymerization onto the precipitated polymers they produce.<sup>8,626</sup> Several attempts with this self-immobilizing approach were made using phenoxy-imine Ni<sup>266,267</sup> or group 4 metal<sup>170,449</sup> complexes **420** (Chart 38) or **121** (Chart 10), having allyl or allyloxy groups. These complexes were reported to afford PEs with improved morphology (bulk density: 0.15–0.28 g/mL)<sup>170,266</sup> but with very large PDI values. Immobilization of a Zr complex (**121**: M = Zr, R<sup>1</sup> = 4-(allyl-O)C<sub>6</sub>H<sub>4</sub>, R<sup>4</sup> = H) on a mesoporous zeolite (SBA-15) pretreated with MAO yielded fiberlike PEs, of which the diameters were about 60 nm.<sup>207</sup> Similarly, a Zr complex **421** on MCM-41/MAO furnished a supported catalyst, which showed lower but more stable activities than the homogeneous

Chart 39



catalyst in ethylene polymerization.<sup>93</sup> The PE obtained possessed higher molecular weights, larger PDI values, and a partly fiberlike morphology (10–100 nm in diameter).

Fujita and co-workers employed a heteropolyacid modified with Ph<sub>3</sub>CCl as an activator for bis(phenoxy-imine) Zr complexes.<sup>627</sup> A bis(phenoxy-imine) Zr complex **85** with the heteropoly compound (Ph<sub>3</sub>C)<sub>m</sub>H<sub>n</sub>[PMo<sub>12</sub>O<sub>40</sub>]·8H<sub>2</sub>O (*m/n* = 2:1 on average) and Et<sub>3</sub>Al afforded PE (*M<sub>w</sub>* = 30 kg/mol, *M<sub>w</sub>/M<sub>n</sub>* = 1.45) at a high activity of 5.64 kg-polymer/(mmol-M·h·bar).

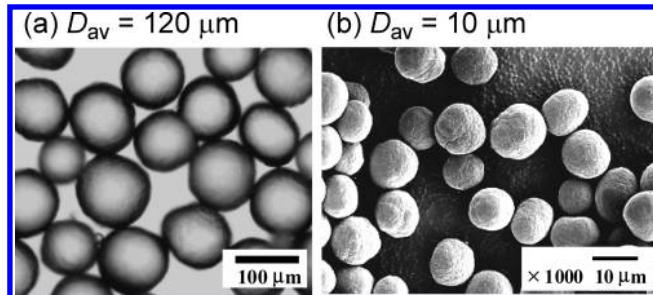
Klapper and co-workers prepared polystyrene latex supports furnished with pyridyl groups (by copolymerization of 4-vinylpyridine) and poly(ethyleneoxide) as an emulsion stabilizer and used them with a bis(phenoxy-imine) Ti complex **422** in ethylene polymerization. The latex-supported catalysts afforded ultrahigh molecular weight PE with relatively narrow molecular weight distributions (*M<sub>w</sub>/M<sub>n</sub>* 2–3) and good morphology (bulk density up to 0.45 g/mL).<sup>164</sup> The supported catalysts exhibited stable activity profiles at >1 kg-polymer/(mmol-M·h·bar) for at least 6 h. In this regard, it was suggested that pyridyl groups might trap Me<sub>3</sub>Al in MAO, which caused irreversible deactivation, as discussed in section 3.4.

## 10. ADVANCED MATERIALS MADE POSSIBLE BY PHENOXY-IMINE COMPLEXES

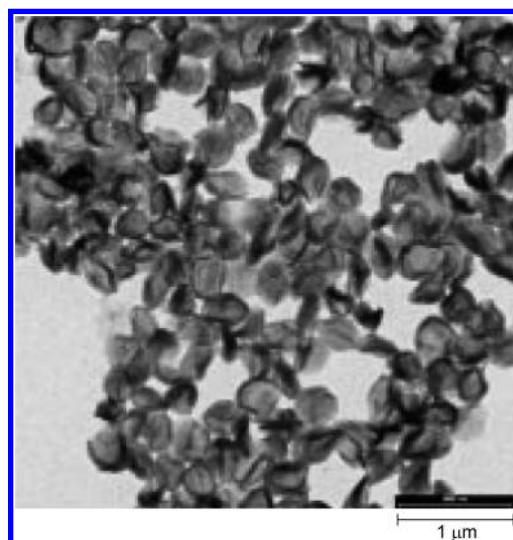
As mentioned in section 1.1, polyolefin resin is the most produced resin in the world today, and polyolefinic materials are ubiquitous in everyday life. One of the reasons for this proliferation is the innate versatility of polyolefins, which stems ultimately from primary molecular structures consisting of components such as structure, combination, composition, alignment, and distribution of monomer units, stereo- and regioregularity, molecular weight and molecular weight distributions, frequency and length of chain branching, chain-end structures, and so on. As reviewed in the sections above, the high degree of freedom for catalyst design and unique structural and electronic characteristics possessed by the phenoxy-imine catalyst family have brought about new polyolefin molecular structures that are unavailable using known catalysts, and the production of new and advanced polyolefinic materials is now an industrial possibility.<sup>628,629</sup>

### 10.1. Ultrahigh Molecular Weight Polyolefins

Ultrahigh molecular weight PEs (UHMWPE) in general refer to PEs that possess molecular weights of 1.5 million or higher. UHMWPE possess excellent tribological property, abrasion resistance, impact resistance, and chemical resistance, and they have applications such as modifiers for resin



**Figure 12.** (a) Photograph and (b) SEM image of spherical particle PEs. Reproduced with permission from ref 27. Copyright 2009 American Chemical Society.



**Figure 13.** TEM micrograph of latex particles. Reproduced with permission from ref 68. Copyright 2001 Wiley-VCH Verlag GmbH & Co. KGaA.

and rubber, porous compacts (sintered filters, etc.), antifriction materials, artificial bones, prosthetic limbs, additives for foaming resin, and so on.

Group 4 metal phenoxy-imine catalysts can produce UHMWPE. For example, a prototypical Zr complex **62** with iBu<sub>3</sub>Al/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] yielded UHMWPE (*M<sub>v</sub>* > 5,000,000 g/mol) under atmospheric ethylene at 50 °C with an activity of 11 kg-polymer/(mmol-M·h·bar).<sup>24,26,205,408</sup> The Zr complexes bearing sterically demanding R<sup>1</sup> (= 2-methylcyclohexyl) gave UHMWPE (*M<sub>v</sub>* 2–5 × 10<sup>6</sup> g/mol) with MgCl<sub>2</sub>/iBu<sub>m</sub>Al(OR)<sub>n</sub> or MAO at extremely high activities of 750–1800 kg-polymer/(mmol-M·h) under industrially viable conditions (50 °C, 0.9 MPa ethylene pressure).<sup>516,517,609</sup>

Alternatively, living N-perfluorophenyl phenoxy-imine Ti catalysts can unsurprisingly produce very high molecular weight PEs;<sup>166,630</sup> however, determination of molecular weight and molecular weight distribution by GPC sometimes becomes unreliable at molar mass >1,000,000 g/mol. PEs produced by a well-controlled living polymerization can provide a useful means to address the problem. A melt rheometrical measurement can determine the high molar mass of linear PEs with reasonably good accuracy, and the measurements demonstrated that complex **56** yielded up to 10<sup>7</sup> molar mass PEs still in a controlled manner.<sup>631</sup>

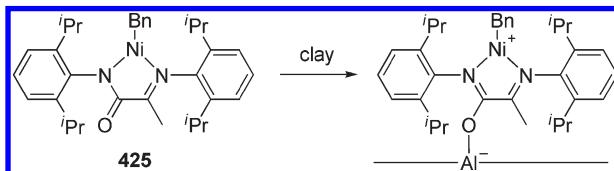
## 10.2. Polyolefin Microparticulates

The morphology of polyolefins not only is critical for efficient production in slurry and gas-phase processes but also is important for some applications, where the polymer products are used as particulates. The morphology of polyolefins is typically regulated by solid polymerization catalysts, whose morphology is enlarged regarding the resulting polymers that are larger in size but similar in shape (in other words, catalyst morphology is replicated to that of polymers). As described in section 9.2,  $MgCl_2$  plays dual roles, a catalyst support and an activator, in olefin polymerizations mediated by phenoxy-imine ligated or, maybe in a more general sense, heteroatom ligated transition metal complexes. The morphology of  $MgCl_2$  can be regulated in spherical shapes with variable size and narrow size distribution via established dissolution/reprecipitation processes. The  $MgCl_2$  supports, when combined with bis(phenoxy-imine) group 4 metal complexes, furnished high molecular weight PE particulates with good morphology.<sup>516,517,609,614,615</sup> With the most sophisticated  $MgCl_2$  supports and complex 423 (Chart 39), Fujita and co-workers synthesized noncoherent UHMWPE particulates ( $M_v > 3,000,000$  g/mol) having uniform spherical shape and very high bulk density of 0.50 g/mL with variable diameters (Figure 12). These UHMWPE particulates are expected to have a wide array of applications in sintered sheets and filters, light diffusion films, high performance resin modifiers and cosmetics, and so on.

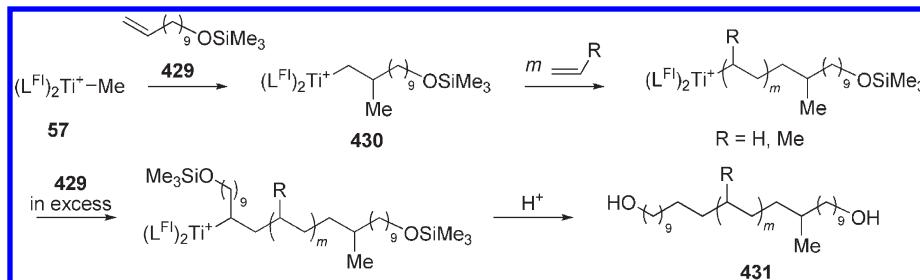
An alternative way to produce polyolefin particulates is via dispersion and emulsion polymerizations, which are usually carried out in organic solvents/water biphasic systems and have been widely employed in radical polymerization. As discussed in section 9.3, Mecking and co-workers revealed that phenoxy-imine Ni complexes can be applicable to water-based emulsion polymerization, furnishing polyolefin latexes that are unavailable via radical polymerizations (Figure 13).<sup>67–72,74–76,202,300,301,303</sup> The applications of polyolefin latexes will be environmentally benign and nonflammable coatings, paints, adhesives, and many others.<sup>620</sup>

Mecking and co-workers also prepared silica/PE nanocomposites by mini-emulsion polymerization in the presence of silica nanoparticles (40–90 nm by TEM).<sup>71</sup> Only when the surface of the silica was hydrophobically modified by trimethoxy-

**Scheme 34**



**Scheme 35**



(7-octen-1-yl)silane, or trimethoxy(*n*-octyl)silane were the silica nanoparticles embedded at the periphery of the semicrystalline PE particles, which were formed by a Ni complex 424. When amorphous PE was synthesized by a Ni complex 69 in Chart 8, surface modification with the polymerizable octenyl group was necessary to obtain the nanocomposites.

Similarly, Scott and co-workers synthesized nanocomposites of clay and polyolefin by using acid-treated montmorillonite.<sup>632</sup> Again, when the catalysts employed were supposed to have a strong interaction with the surface of the clay, such that complex 425 could form a zwitterionic species at the Lewis acidic Al on the surface (Scheme 34), a highly dispersed composite material was obtained. The other complexes including a bis(phenoxy-imine) Ti complex, which had little such interaction, furnished PEs with the nonuniformly dispersed clay.

As already discussed in section 9.4, PE nanofibers can be generated by zeolite-supported catalysts, supposedly due to the polymerization taking place in the mesoporous linear channels of the zeolites.<sup>93,207</sup>

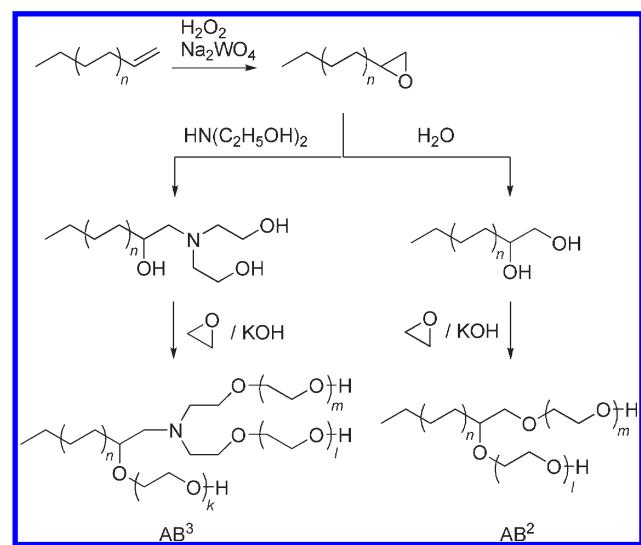
## 10.3. Functionalized Polyolefins

Introduction of polar functional groups to nonpolar polyolefins is one way to expand the application of polyolefinic materials because it gives them properties such as adhesivity, dyeability, printability, and compatibility with other polar materials. Functionalized polyolefins can also be a reactive precursor for polyolefin hybrid materials in combination with other materials also having complementary reactive groups. However, the chemical stability of polyolefins and general incompatibility of olefin polymerization catalysts with polar functional substrates have restricted functionalized polyolefins to relatively limited commercial applications, most of which are based on radical grafting or radical polymerization technology.

The advent of post-metallocene catalysts has significantly expanded the scope for synthesis of functionalized polyolefins, for which a number of reviews are available.<sup>543,633</sup> In this section, functionalized polyolefins prepared by phenoxy-imine based catalysts are summarized with regard to (1) side chain functionalities and (2) chain-end functionalities.

**10.3.1. Side Chain Functionalities.** Copolymerization of olefins and polar functional monomers is the most straightforward way to prepare polyolefins that have pendant functional groups. The major and common approach has been to use masked polar comonomers to minimize the poisoning of catalysts by such functional groups.<sup>65,389</sup> More recently, high performance late transition metal catalysts that tolerate functional groups have been successful in copolymerizing a variety of polar comonomers (see section 4.2.3). Moreover, Fujita and co-workers have demonstrated that bis(phenoxy-imine) Ti complexes can polymerize ethylene with an ester functionalized olefin under

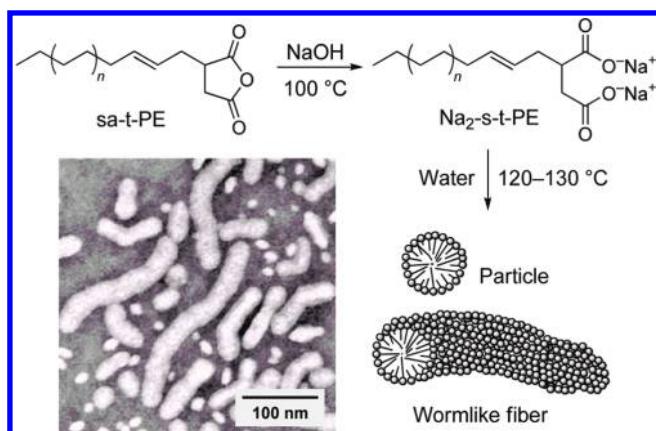
Scheme 36



the conditions where the polar monomer was excess to the added MAO (see section 4.1.3.3). By using a Ti complex **296** ( $Ar = Ph$ ) bearing a tridentate  $[O,N,S]$  ligand, Tang and co-workers synthesized copolymers having dangling phosphine groups along the PE main chain (3.9 mol %), which serves as a recoverable and reusable catalyst for [3+2] cycloaddition reactions.<sup>533</sup>

An alternative approach to prepare side chain functionalized polyolefins is the copolymerization of ethylene and a nonconjugated diene and subsequent functionalization of the residual double bonds. Tang and co-workers prepared ethylene/DCPD copolymers by a Ti complex **299** bearing a tridentate  $[O,N,S]$  ligand, whose remaining double bonds in a five membered ring were quantitatively epoxidized with *m*-chloroperbenzoic acid.<sup>116</sup> Similarly, Li and co-workers synthesized functionalized polyolefins from poly(ethylene-*co*-norbornadiene) and poly(ethylene-*co*-DCPD) obtained with  $(L^{KI})_2TiCl_2$  (**363**, **426**, **427**)/MMAO via known organic synthetic approaches, i.e., epoxidation and hydroboration.<sup>563</sup> Furthermore, block copolymers, PE-*b*-poly(ethylene-*co*-DCPD), prepared by the complex **426** were also functionalized using similar methods.<sup>185</sup> Bao and co-workers prepared poly(NBE-*co*-1,4-divinylbenzene) with complex **428** and tried to synthesize graft copolymers of MA<sup>588</sup> and MMA<sup>587</sup> via atom transfer radical polymerization using pendant  $-C_6H_4-CH=CH_2$  groups as a hold of the grafting reaction. Coates and co-workers polymerized 1,5-hexadiene (HD) using complex **152**/MAO in a living manner, resulting in polymers that had 1,3-methylenecyclopentane (MCP) and 3-vinyltetramethylene (VTM) units in the main chains with narrow molecular weight distributions.<sup>634</sup> The MCP units were derived from 1,2-insertion of HD followed by intramolecular cyclization, and the VTM units came presumably from 2,1-insertion of HD, intramolecular cyclization forming methylene cyclobutane units, and subsequent rearrangement of the strained methylene cyclobutane units via  $\beta$ -alkyl elimination. The resulting vinyl side chains were not involved in polymerization (no cross-linking) and thus will be available for further functionalization. An application of this polymer as a photonic crystal was introduced in section 10.4 below.

**10.3.2. Chain-End Functionalities.** Fujita and co-workers prepared chain-end-functionalized polyolefins using a living bis(phenoxy-imine) Ti catalyst **56** and  $\omega$ -functionalized  $\alpha$ -olefins

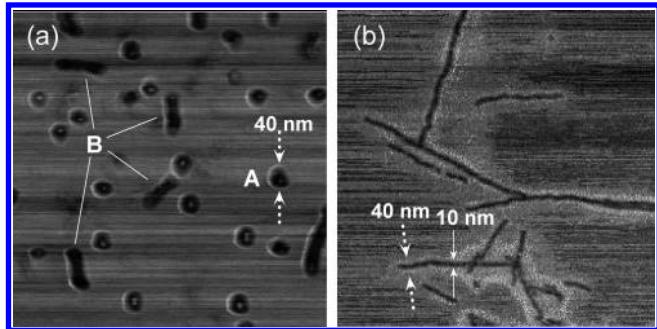


**Figure 14.** Synthetic scheme and TEM image of a  $Na_2$ -s-t-PE water dispersion. Reproduced with permission from ref 639. Copyright 2009 American Chemical Society.

(for example,  $H_2C=CH(CH_2)_9OSiMe_3$  (**429**) (Scheme 35)).<sup>635</sup> Because complex **56**/MAO furnished a highly active and robust living polymerization catalyst **57**, but extremely slow in consecutive insertions of large  $\alpha$ -olefins such as **429**, an equimolar amount of **57** and **429** yielded a functional initiator **430**, which of course served as a highly active and robust living polymerization catalyst. Chain-end-capping was also carried out using **429** to produce telechelic polyolefin **431** after quenching. Again, the functionalization is quantitative due to the slow consecutive insertions of **429**.

Chain-end functionalities can also be incorporated via chain transfer reactions. By using main group metal alkyls ( $M'-R$ ) or hydrides as a chain transfer agent, one can synthesize polyolefins having carbon-M' bonds at the chain termini. The reactive C-M' moieties can be utilized to introduce functional groups via postpolymerization reactions.<sup>636</sup> Alternatively,  $\beta$ -H transfer reaction yields polyolefins with unsaturated chain ends. Selective functionalization at chain ends with  $-AlMe_2$ <sup>414</sup> or vinyl groups<sup>214,220,222</sup> was possible with bis(phenoxy-imine) group 4 metal complexes through understanding of chain transfer mechanisms and judicious design of ligand structures (see section 4.1.1.2). Fujita and co-workers demonstrated that the addition of  $H_2$  or  $Et_2Zn$  released the propagating polymer chains from living bis(phenoxy-imine) Ti catalysts via chain transfer reactions and then the Ti species could reinitiate a living polymerization by additional monomer supply without being disturbed by the presence of chain transfer agents.<sup>26,372,637</sup> When  $Et_2Zn$  was used as a chain transfer agent, PEs having narrow molecular weight distributions and Zn-C bonds at the chain termini were obtained. Gibson and co-workers demonstrated that in this case  $Et_2Zn$  can serve as a reversible chain transfer agent for some olefin polymerization catalysts, including Hf and Cr complexes bearing phenoxy-imine ligands.<sup>538</sup> When the chain transfer to R-Zn (R: alkyls or polymethyl) moieties is reversible and fast relative to propagation, every R-Zn species has an equal opportunity on average to enter the catalytic chain growth via reverse chain transfer to the catalyst, resulting in uniform length of polymer chains (a Poisson distribution). This catalytic chain growth on zinc afforded zinc terminated ethylene oligomers ( $M_n \sim 10^3$  g/mol) with narrow molecular weight distributions, which were transformed into primary alcohols and  $\alpha$ -olefins via oxidation and olefin displacement, respectively.<sup>638</sup>

Fujita and co-workers demonstrated that vinyl terminated PEs prepared by bis(phenoxy-imine) Zr complexes bearing



**Figure 15.** Phase mode AFM image, scan area:  $700 \times 700 \text{ nm}^2$ , (a) round shape structures, A: individual unit, B: assembled units. (b) rodlike structures. Reproduced with permission from ref 491. Copyright 2003 The Chemical Society of Japan.

small R<sup>1</sup> groups (see section 4.1.1.2) could be converted to a variety of functionalized PEs. For instance, by oxidation with H<sub>2</sub>O<sub>2</sub> using Na<sub>2</sub>WO<sub>4</sub> as a catalyst, a vinyl terminated PE was readily converted to the corresponding epoxy-terminated PE in a practically quantitative yield. The epoxy-terminated PEs were highly reactive and could be transformed into, for example, a diol-terminated PE by the in situ hydrolysis using aqueous 2-propanol or a triol-terminated PE via the reaction with diethanolamine.<sup>214,220,413</sup> The diol- or triol-terminated PEs can serve as a building block for well-defined hybrid materials of PE and polyethylene glycol (PEG) having AB<sup>2</sup> and AB<sup>3</sup> block structures (Scheme 36).<sup>412,413</sup> These hybrid materials formed a stable water dispersion (up to 40 wt % of the hybrid materials) without the need for surfactants. Particularly, the AB<sup>3</sup> hybrid (PE, M<sub>n</sub> 1100 g/mol; PEG, average M<sub>n</sub> 400  $\times$  3 g/mol, T<sub>m</sub> 120 °C) formed a semitransparent dispersion, consisting of nanoparticles (~18 nm on average) with a narrow size distribution. The nanoparticles can encapsulate large organic molecules, for example, 2,7,12,17-tetra-*tert*-butyl-5,10,15,20-tetraazaporphyrinato copper(II) (a water-insoluble dye) or 8-anilino-1-naphthalene sulfonic acid (a probe showing no fluorescence in a hydrophilic environment), indicating that the nanoparticles have very lipophilic PE cores with hydrophilic shells of PEG.

Conversely, the Alder-ene reaction of vinyl-terminated PE with maleic anhydride in the presence of nitrobenzene or 2,6-di-*tert*-butyl-4-methylphenol yielded the corresponding succinic anhydride-terminated PE.<sup>639</sup> The succinic anhydride-terminated PE (sa-t-PE) exhibited higher melt viscosity and higher thermal stability than the parent vinyl-terminated PE due to the presence of the chain-end succinic anhydride group. Interestingly, the Na salt of this succinic anhydride-terminated PE (Na<sub>2</sub>-s-t-PE) formed nanosized particles (diameter 10–30 nm) and wormlike fibers (fiber diameter 20–30 nm, length 60–270 nm) (Figure 14) as self-assemblies in water.

#### 10.4. Olefin Block Copolymers

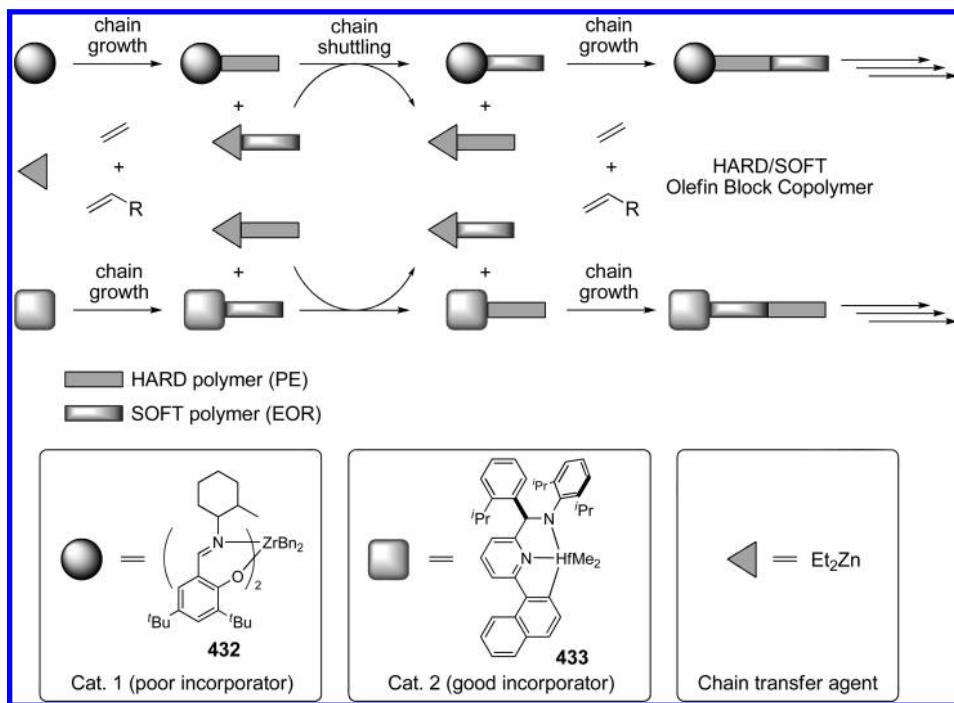
As discussed in section 4.1, the advent of highly active, robust, and versatile living olefin polymerization catalysts based on phenoxy-imine ligated complexes has significantly widened the range of olefin block copolymers and has enabled synthesis of block copolymers with well-defined structures (Table 26). One of the advantages of block copolymers lies with the higher order structures that they can form via microphase separation.<sup>640</sup> Therefore, the morphology of a single molecule of block copolymers and their higher order structures in bulk are of great interest because these structures eventually cause whatever properties the block copolymers may possess.

The morphology of a presumably single molecule of diblock copolymers, PE-*b*-EPR, on mica was directly observed by atomic force microscopy (AFM).<sup>491</sup> A round shape structure attributable to a single molecule appeared to consist of a small PE core (2.5–5.0 nm  $\times$  5.0–10.0 nm) surrounded by a thick EPR shell (~40 nm in diameter) (Figure 15a). The structure coincides with a small-angle neutron scattering (SANS) study on PE-*b*-EPR (prepared by anionic polymerization of butadiene and isoprene followed by hydrogenation), which revealed similar core-brush structures in decane solution.<sup>641</sup> In addition to the round structure, rodlike structures were also observed on mica, which possessed a PE center core in a EPR sheath apparently in similar dimensions to the round structure, suggesting that several of the round structures were aggregated into the rod structures (Figure 15b). Radulescu and co-workers investigated the self-assembly of sPP-*b*-EPR in solution using SANS.<sup>492</sup> The sPP-*b*-EPR blocks yielded one-dimensional aggregates with a radii of about 44 and 80 nm, depending on the molecular weights of the block copolymers, and the aggregates were self-assembled into bundle and network-like supramolecular structures on a larger scale. With regard to phase behavior in bulk, it was shown that block copolymers, including sPP-*b*-EPR,<sup>426,493,642</sup> sPP-*b*-PE,<sup>493</sup> and sPP-*b*-EPR-*b*-sPP,<sup>643</sup> can have a variety of ordered or disordered (random) morphologies.

Fujita and co-workers successfully prepared a series of diblock copolymers consisting of PE and poly(ethylene-*co*- $\alpha$ -olefins) ( $\alpha$ -olefins: 1-hexene, 1-octene, 1-decene) with well-defined structures using complex 177.<sup>407</sup> For these diblocks, thermal and mechanical properties were investigated in relation with the block structures. When the second poly(ethylene-*co*-1-hexene) (EHR) blocks that differed in length (1-hexene ~8 mol %, M<sub>n</sub> 23,000–83,000 g/mol) were attached to a monodisperse PE (M<sub>n</sub> 38,300 g/mol, PDI 1.11, T<sub>m</sub> 135 °C), the melting temperatures were progressively dropped with the increase of EHR molecular weights. When the second EHR blocks were varied in 1-hexene contents at an almost constant length (1-hexene 8.3–28.9 mol %, M<sub>n</sub> 42,000–48,000 g/mol), an increase of the melting temperatures was observed with 1-hexene contents. Furthermore, tensile tests on a PE-*b*-EHR sample exhibited better extensibility and toughness in comparison to the corresponding random copolymer and the polymer blend. Coates and co-workers prepared sPP-*b*-EPR-sPP triblock copolymers using Ti complex 152. The block copolymers had a microphase-separated morphology consisting of sPP cylinders in an EPR matrix at the weight fraction of sPP < 0.3, whereas, at the weight fraction of sPP > 0.5, sPP became a continuous phase. The block copolymers that had an EPR matrix demonstrated elastomeric behavior, which was comparable to or better than that of commercial polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) triblock copolymers.<sup>643</sup> They also employed bis(phenoxy-ketoimine) Ti complex 169 with MAO in order to synthesize tri-, penta-, and hepta-block copolymers having iPP and EPR segments, iPP-*b*-EPR-*b*-iPP, iPP-*b*-EPR-*b*-iPP-*b*-EPR-*b*-iPP, and iPP-*b*-EPR-*b*-iPP-*b*-EPR-*b*-iPP-*b*-EPR-*b*-iPP. These block copolymers also exhibited excellent mechanical properties as thermoplastic elastomers even in cases where disordered random morphology was observed.<sup>91,643</sup>

Thomas, Coates, and co-workers demonstrated that poly-(MCP-*co*-VTM)-*b*-poly(ethylene-*co*-NBE) and EPR-*b*-poly(ethylene-*co*-NBE)<sup>634</sup> were self-assembled in a lamellar morphology, exhibiting a partial 1-D photonic band gap with an excellent

Scheme 37



optical transparency, of which optical properties can be tuned by blending homo- or random (co)polymers.<sup>494</sup>

All block copolymers described above were synthesized by living polymerizations, and therefore, 1 mol of catalyst molecules can produce essentially 1 mol of polymer chains, which imposes a crucial limitation in terms of polymer productivity. Scientists at Dow Chemical Co. recently addressed a solution to this problem using a catalytic chain growth on zinc described above.<sup>644–649</sup> If two catalysts that have very different comonomer reactivity ratios (Cat. 1, poor comonomer incorporator; Cat. 2, good comonomer incorporator) are mixed together, and if both catalysts are subject to rapid and reversible chain transfer reactions, polymer chains having different comonomer compositions can be swapped between two different catalysts and subsequent chain growth on each catalyst will make a covalent bond between the two different polymer segments (Scheme 37). It was found using a high throughput screening method that a zirconium (phenoxy-imine) complex **432**, which was highly selective toward ethylene enchainment relative to 1-octene (see section 4.1.3.1), and a hafnium pyridylamide complex **433**, which incorporated a significant amount of 1-octene in ethylene/1-octene copolymerization (that made elastic soft segments having  $T_g < -40^\circ\text{C}$ ), produced multi-block copolymers having PE and poly(ethylene-*co*-1-octene) (EOR) segments in the presence of Et<sub>2</sub>Zn as a reversible chain transfer agent. Significantly, they also revealed that this dual-catalyst system with reversible chain transfer, named “chain shuttling polymerizations”, worked even better in a continuous polymerization reactor, which can be easily scaled into industrial production at existing plants.

The multiblock copolymers (PE-*b*-EOR)<sub>n</sub> exhibited high  $T_m$  ( $>120^\circ\text{C}$ ) due to the existence of PE segments despite a significant 1-octene incorporation,<sup>644</sup> and they showed characteristic thermoplastic elastomer behavior because the hard PE segments served as physical cross-linking points.<sup>650</sup> Hiltner and co-workers carried out an extensive study on the relationships between primary and secondary structures of (PE-*b*-EOR)<sub>n</sub> and their

properties as thermoplastic elastomers.<sup>651–653</sup> Regarding adhesion to PP, (PE-*b*-EOR)<sub>n</sub> was consistently better than random EOR.<sup>654</sup> The morphology and phase behavior of polymer blends including (PE-*b*-EOR)<sub>n</sub> were also investigated.<sup>655</sup> Hsiao and co-workers investigated deformation processes of (PE-*b*-EOR)<sub>n</sub> using *in situ* synchrotron X-ray scattering and diffraction techniques.<sup>656</sup>

## 11. CONCLUDING REMARKS

Transition metal mediated olefin insertion polymerization catalysts have evolved dynamically over the past 60 years, and they have been the main driver behind the development of the polyolefin industry. And in the past decade or so, the development of the ligand oriented catalyst design concept emphasizing the flexible electronic nature of a ligand (as introduced in section 1.2) has brought forth into focus the fact that the history of olefin polymerization catalysts is, in a sense, the search for and development of ancillary ligands. Well-defined discrete molecular catalysts equipped with appropriately designed organic ligands have allowed scientists to understand and even control the reactivity and the selectivity of olefin polymerizations in a rational manner, which was impossible with the traditional Ziegler–Natta catalysts supported on the ill-defined inorganic surfaces that served as a part of their ligands. That is why the discovery of metallocene catalysts is such a big breakthrough within the development of olefin polymerization catalysis.

post-metallocene catalysts that followed metallocene catalysts have offered further diversity and opportunities for the development of olefin polymerization catalysis in that they have sterically and electronically offered a much higher degree of freedom for catalyst design than metallocene catalysts.

Among the post-metallocene catalysts developed, phenoxy-imine ligands possess a particularly large diversity of structures because of their straightforward synthesis and modular properties.

Due to these diversified structures, the progress in phenoxy-imine based catalyst development has been remarkable, as discussed in this comprehensive treatment.

In addition, upon complexation within the phenoxy-imine framework, the substituents (particularly R<sup>1</sup> and R<sup>2</sup>) are suitably situated around the metal center for strategically controlling the polymerization reactions. Furthermore, phenoxy-imine ligands are structurally flexible due to the labile imine donors and, therefore, can be electronically flexible, too, allowing phenoxy-imine ligands to show both electron-receptive and electron-donating properties, depending on the state of the metal center. These inherent features pertaining to phenoxy-imine ligands have resulted in their great aptitude to be olefin polymerization catalysts independent of the early to late transition metal centers.

As discussed in detail in this comprehensive treatment, the diversity and versatility of phenoxy-imine complexes is what lies behind the creation of new olefin polymerization reactions and novel polyolefinic materials, something that was difficult or impossible to achieve with other known catalysts. It is hoped that phenoxy-imine and other advanced catalysts will continue to furnish new and useful polyolefin products that meet the social and environmental demands of the modern world and, at the same time, enhance our understanding of the causal sequences between catalyst structures, polymerization characteristics, primary and higher order polymer structures, and the chemical and physical properties of the resultant materials.

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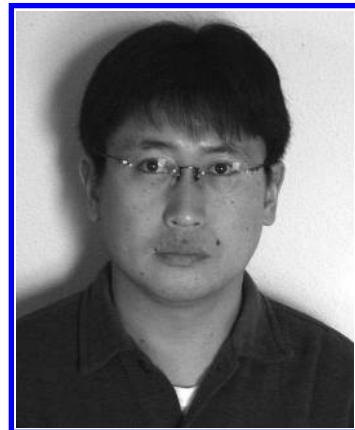
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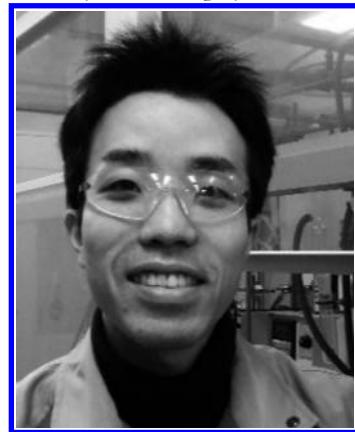
## BIOGRAPHIES



Haruyuki Makio received his B.S. and M.S. degrees in polymer chemistry from Kyoto University under the direction of Professors Toshinobu Higashimura and Toshio Masuda. He joined Mitsui Petrochemical Industries, Ltd. (now Mitsui Chemicals, Inc.) in 1992 as a researcher, where he is working on development of new olefin polymerization catalysts and new polyolefinic materials. In 1999–2001, he was a visiting scholar under Professor Tobin J. Marks at Northwestern University. He received the Kinki Chemical Society Award for Chemical Technology in 2008. He earned his Ph.D. from Kyoto University in 2011.



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## GLOSSARY

$[\eta]$	intrinsic viscosity
Ac	acetyl group
acac	acetylacetone
acen	$N,N'$ -bis(acetylacetone)ethylenediamine
Adm	adamantyl
aPP	atactic polypropylene
b	block
Bn	benzyl
CGCs	constrained geometry Cp-amido complexes
CGC	$\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}^{\text{i}}\text{Bu})\text{TiCl}_2$
<i>co</i>	copolymer
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl, $\text{C}_5\text{H}_5$
Cp'	the generic form of cyclopentadienyl or its substituted derivatives
Cp*	pentamethylcyclopentadienyl, $\text{C}_5\text{Me}_5$
Cy	cyclohexyl
$D_{\text{av}}$	average particle diameter
dba	dibenzylideneacetone
DCPD	dicyclopentadiene
DFT	density functional theory
DMAO	dried methylaluminoxane, from which trimethylaluminum is removed in vacuo
DME	1,2-dimethoxyethane
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
EAO	ethylaluminoxane
EBR	poly(ethylene- <i>co</i> -but-1-ene) rubber
EPR	poly(ethylene- <i>co</i> -propylene) rubber
ETA	ethyltrichloroacetate ( $\text{CCl}_3\text{COOC}_2\text{H}_5$ )
GPC	gel permeation chromatography
HDPE	high-density polyethylene
iPP	isotactic polypropylene
iPS	isotactic polystyrene
LDA	lithium diisopropylamido

LLDPE	linear low-density polyethylene
<i>m</i>	meso diad
M	transition metals
$M'$	main group metals
MA	methyl acrylate
MAO	methylaluminoxane
Mes	mesityl
MMAO	modified methylaluminoxane
MMA	methyl methacrylate
$M_n$	number-average molecular weight
$M_v$	viscosity-average molecular weight
$M_w$	weight-average molecular weight
NBE	norbornene
NHC	N-heterocyclic carbene
PDI	polydispersity index, $M_w/M_n$
PE	polyethylene
PEG	polyethylene glycol
PP	polypropylene
PS	polystyrene
PTS	<i>p</i> -toluenesulfonic acid
py	pyridine
<i>r</i>	racemo diad
$r_1$	the monomer reactivity ratio of $M_1$ in copolymerization of two monomers, $M_1$ and $M_2$
sPP	syndiotactic polypropylene
sPS	syndiotactic polystyrene
TEM	transmission electron microscopy
$T_g$	glass transition temperature
THF	tetrahydrofuran
$T_m$	melting temperature
TMEDA	$N,N,N',N'$ -tetramethylethylenediamine
TOF	turnover frequency
TON	turnover number
UHMWPE	ultrahigh molecular weight polyethylene

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