

# Designing late-transition metal catalysts for olefin insertion polymerization and copolymerization

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The innovation of polyolefin with unique architecture, composition and topology continues to inspire polymer chemists. An exciting recent direction in the polyolefin field is the design of new catalysts based on late-transition metals. In this review, we highlight recent developments in rationally designing late-transition metal catalysts for olefin polymerization. The examples described in this review showcase the power of the design of well-defined late-metal catalysts for tailored polyolefin synthesis, which may usher in a new era in the polymer industry.

## 1. Introduction

Polymeric materials, including plastics, fibers, and elastomers, play an essential role in our life. Polyolefins are an important family of polymers, with billions of pounds produced annually.<sup>1</sup> Given the abundance and low cost of olefinic monomers from the petroleum industry, it is particularly attractive to develop efficient polymerizations to transform these simple monomers into novel polymeric materials. The range of polyolefin products will grow steadily to meet the increasingly sophisticated needs of consumers.<sup>2</sup> The industry therefore requires constant innovation of novel polymer structures for new applications. To meet this goal, it is essential to *continuously discover and develop new polymerization chemistry*. This industrial imperative is aptly

echoed in the general roadmap proposed by the Council of Chemical Research for achieving what is referred to as the Vision 2020 Catalysis<sup>3</sup> goals. The “identification of methods for achieving control of polymer architecture and composition” is one of the targets in the area of polymerization. This goal calls for a “new catalyst design through combined experimental, mechanistic understanding, and improved computational modeling of catalytic processes” for the advancement of polymerization chemistry. An exciting research effort in this direction is the design and development of new catalytic systems that efficiently convert common olefin feedstock into high value polymeric materials.<sup>4</sup>

Historically, the design of new catalysts for olefin polymerization has mostly focused on early transition metals.<sup>5</sup> Recently, however, there has been a renaissance in the development of late-transition metal-based systems.<sup>6</sup> In the last decade, a variety of well-defined late-transition metal complexes with specific catalytic properties have been designed to afford polymers with unique architectures.<sup>7</sup> Through highlighting recent examples from others’ and our own laboratory, this article briefly reviews the evolution in designing late-transition metal catalysts for insertion polymerization and

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copolymerization of relatively simple olefins. The scope of this review is limited to single-site, homogenous, late-transition metal polymerization catalyst systems. For many other interesting late-metal complexes, including heterogenous systems,<sup>8</sup> binuclear systems,<sup>9</sup> and catalysts that polymerize dienes,<sup>10</sup> cyclic olefins,<sup>11</sup> allenes,<sup>12</sup> norbornenes<sup>13</sup> and styrenes,<sup>14</sup> the readers are referred to excellent reviews as cited.

## 2. Historical development of late metal polymerization catalysts

The development of olefin polymerization catalysts began with the chemistry of late-transition metals. The seminal discovery of the Ziegler–Natta catalysts can be traced back to the serendipitous observation of the so-called “Nickel-effect” by Karl Ziegler.<sup>15</sup> In carrying out the ethylene oligomerization reaction (“Aufbaureaktion”) using aluminium trialkyls, Ziegler and coworkers observed that an adventitious amount of nickel, which was leached out of the reactor alloy due to acid washing, in combination with aluminium trialkyls, led to the formation of 1-butene. This Nickel-effect demonstrates clearly how traces of transition metals could radically alter the reaction between an olefin and a main-group organometallic. The catalytic nature of the nickel species was recognized years later<sup>16</sup> to involve a multicenter bonding system between nickel(0) and the organoaluminium. This serendipitous observation spurred a comprehensive screening of the activities of other transition metals across the periodic table. From this intense effort, it was discovered that TiCl<sub>4</sub> or ZrCl<sub>4</sub> in combination with aluminium trialkyls could produce high molecular weight (MW) polyethylene (PE) at high activities. Shortly thereafter, the potential of this catalytic system was significantly expanded when Natta *et al.* prepared and characterized isotactic polypropylene using similar catalyst systems.<sup>17</sup> Ziegler and Natta’s work led to the rapid commercialization of the Ziegler–Natta catalysts for production of high molecular-weight polyolefins.<sup>18</sup>

Despite their paramount importance for the manufacture of polyolefins, Ziegler–Natta catalysts have a number of limitations. For example, their heterogenous nature hinders investigation of the fine reaction mechanism and impedes true rational design of new catalysts. Moreover, their multiple catalytic sites lead to non-uniform incorporation of comonomers in copolymers and give mixtures of polypropylenes with different tacticities. To address these issues, the next major breakthrough of olefin polymerization catalysis is the development of homogenous early Metallocene systems.<sup>19</sup> These Metallocene catalysts allow the production of polyolefins with much more precise control of the polymer structure.<sup>20,21</sup> It gives polymers with low polydispersities and allows more uniform incorporation of  $\alpha$ -olefin comonomers. For stereospecific polymerization of  $\alpha$ -olefins, chiral metallocenes have provided an unprecedented level of control of polymer tacticity.<sup>22,23</sup> Most importantly, the homogenous and single-site feature of Metallocene systems opens the age of truly rational design of new polymerization catalysts.<sup>24</sup>

Nevertheless, early-transition metal catalysts suffer from one major drawback, *i.e.*, they generally cannot tolerate polar functional groups because of their highly electron-deficient nature.

This limits their applicability to copolymerization of polar olefins in order to produce more valuable polyolefin products. In addition, despite the exquisite control of composition and tacticity, the architecture of polyolefins prepared by early-transition metal catalysts is mostly linear. For many applications, non-linear topologies, such as hyperbranched, cyclic, dendritic, and core–shell architectures, are interesting to pursue. It would be important to develop transition metal catalyzed polymerizations to provide efficient synthesis of polymers having these new architectures.<sup>25</sup> To overcome the limitations of early-transition metal catalysts, there has been a major shift of focus to late-transition metal systems in the recent development of new olefin polymerization catalysts.

### 2.1 Early development of late metal polymerization catalysts

Late-transition metals have been employed in the Shell Higher Olefin Process (SHOP) in the oligomerization of ethylene for high olefin synthesis. The design of SHOP catalysts, such as **1** and **2** (Fig. 1), is based on the ability of late-transition metals to undergo facile  $\beta$ -hydride elimination to afford low molecular weight oligomers. This feature is the basis of the successful oligomerization of ethylene for the manufacture of surfactants, lubricants, and fine chemicals. Whereas most of the early generations of late-transition metal catalysts produce linear oligomers, the complex **3** gave a uniquely branched microstructure.<sup>26</sup> This unusual property indicates that late metals can potentially be utilized in the synthesis of polymers whose architecture and branching is different from simple ethylene.

In addition to ethylene oligomerization, SHOP-type catalysts have also been shown to be effective for olefin polymerization. The Ni(II) SHOP catalysts **1** and **2** bearing P–O chelating ligands<sup>27–29</sup> afford polyethylene without the use of a co-catalyst as required in Ziegler-type systems. Under heterogenous conditions, these catalysts can give high MW linear polyethylene,<sup>30</sup> indicating the influence of the reaction medium in controlling MW.<sup>31</sup> The SHOP-type catalyst **4**,<sup>32</sup> bearing a pyridine ligand, and the Co complex **5**,<sup>33</sup> also afford ethylene polymerization. Moreover, catalyst **4** has been shown to copolymerize with some very special polar olefins. It is, however, highly sensitive to common polar olefins. The rhodium catalyst **6**,<sup>34</sup> in contrast, is stable in aqueous suspension, but only enables ethylene oligomerization at extremely low activity.

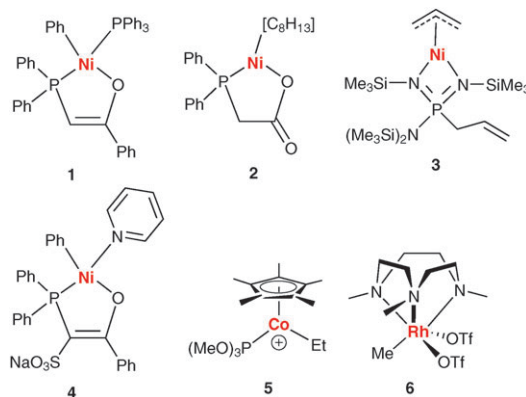


Fig. 1 Representative early examples of late-metal polymerization catalysts.

Nevertheless, these systems are an indication of the tolerance of late-metal catalysts to polar moieties. Despite these few reports, the systems have a serious limitation: they have low activities and they generally gave low MW PE.<sup>35</sup>

## 2.2 General features of late-metal catalysts

Compared to early-transition metals, for a long time late-metal systems were generally perceived to be inferior for high polymerization of olefins due to their facile ability to undergo  $\beta$ -hydride elimination. The prevalent thinking was that late-transition metals can only give low MW oligomers because facile  $\beta$ -hydride elimination should lead to fast chain transfer. Moreover, late-transition metals were perceived to possess inherently lower activities towards olefin insertion compared to early-metal catalysts because the d orbitals of late-metal centers are more filled with electrons and thus less effective for activating an incoming olefin. These presumptions have significantly slowed the development of late-transition metal complexes as catalysts for olefin polymerization.

Despite these perceptions, late-transition metals possess some unique properties that make them potential candidates as catalysts for olefin insertion polymerization. The good functional group tolerance of late-transition metals, as opposed to the highly oxophilic nature of early-metal systems, make it attractive to design late-metal catalysts for copolymerization with functional polar olefins. Early examples of late-metal systems tolerating polar olefins include Pd,<sup>36,37</sup> Ru,<sup>38,39</sup> and Rh<sup>40</sup> complexes, which were shown to dimerize acrylates. Pd(II) catalysts also tolerate carbon monoxide where it copolymerizes with olefins.<sup>41</sup>

One underestimated feature of late-transition metals is that their cationic species can be highly electrophilic. Potentially, they should be able to allow for olefin insertion at a much higher rate than presumed earlier. This characteristic has been explored by Brookhart and coworkers, and the high electrophilicity of cationic late-transition metals was manifest in the high activity of Ni(II)<sup>42</sup> and Fe(III)<sup>43</sup> based catalysts for polymerization of olefins.<sup>44</sup>

Following the seminal work of Brookhart and coworkers in 1995,<sup>42</sup> a variety of late-transition metal complexes have been reported for olefin insertion polymerization over the last decade.<sup>44,45</sup> This article will highlight some important examples of the design of single-site late-transition metal catalysts containing N<sup>+</sup>N<sup>+</sup>, P<sup>+</sup>N<sup>+</sup>, N<sup>+</sup>O<sup>+</sup>, and P<sup>+</sup>O<sup>+</sup> chelating ligands. Due to space limitations, many other exciting late-metal systems, including N-heterocyclic carbene-based systems,<sup>46</sup> metathesis systems,<sup>47</sup> multinuclear catalysts<sup>48</sup> and heterogenous systems,<sup>49</sup> will not be discussed in this article.

## 3. Rational design of late-metal catalysts for olefin polymerization

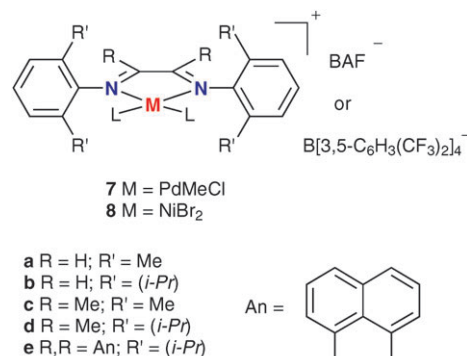
The field of late-metal polymerization catalysis was revitalized by the seminal work reported by Brookhart and coworkers in 1995 on the Ni(II)- and Pd(II)- $\alpha$ -diimine systems.<sup>42</sup> The Ni(II)- $\alpha$ -diimine complexes are highly active and afforded polyethylene with high molecular weight. Interestingly, the Pd(II)- $\alpha$ -diimine complexes convert simple ethylene into highly branched polymers and also allow copolymerization

with polar olefins like methyl acrylate.<sup>50</sup> A key insight gleaned from Brookhart's bis(aryl)- $\alpha$ -diimine system that dispels the previous myth on late metals is that  $\beta$ -hydride elimination does not necessarily lead to chain transfer. By designing bulky  $\alpha$ -diimine ligands to prevent axial association of ethylene, the subsequent olefin displacement—i.e., chain transfer—can be hampered so that high mass polymers can be obtained. Furthermore, the  $\beta$ -hydride elimination and hydride reinsertion reactions can be controlled and utilized for introducing branches into polymers. This is especially demonstrated in the case of Pd(II)- $\alpha$ -diimine catalysts which afforded hyper-branched polymer from simple ethylene. The branching in the polymer results from facile  $\beta$ -hydride elimination and reinsertion reactions. In effect, the Pd “walks” along the chain introducing branches and even branch-on-branch structures. This so-called chain walking mechanism of the Pd(II) system has been employed by our group for rationally controlling the overall architecture and topology of polyolefins, with dendritic polymers being produced at low ethylene pressure.<sup>25,51–53</sup> In the case of Ni(II)- $\alpha$ -diimine catalysts, the more electrophilic nature of Ni favors olefin insertion at a much more competitive rate over  $\beta$ -hydride elimination, thus affording only polymers with short-chain (mostly methyl) branches.

### 3.1 Design of catalyst based on chelating N<sup>+</sup>N<sup>+</sup> ligands

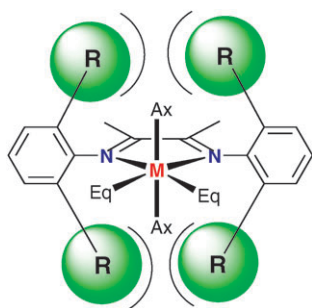
The new Ni(II) and Pd(II) systems reported by Brookhart *et al.* represent elegant examples of rational design of late-metal catalysts for olefin insertion polymerization. These catalysts bear bis(aryl)- $\alpha$ -diimine ligands chelating Pd(II) or Ni(II) metal centers (Fig. 2). Both the high activity of the catalysts and their ability to generate high molecular weight polymers are attributed to the following key features of the catalyst design: the electrophilic and cationic late transition metals (Pd(II) and Ni(II)) as active centers, the sterically bulky  $\alpha$ -diimine as bidentate ligands, and the use of bulky non-coordinating counterions.

The ingenious design of the catalyst exploits the electrophilicity of cationic late-metal centers which allows for rapid olefin insertion. Moreover, the non-coordinating nature of the counterions provides easy access of the incoming olefins to the coordination sites. However, the most important design feature of this system is the incorporation of the sterically



**Fig. 2** Brookhart's Ni(II) and Pd(II) bis(aryl)- $\alpha$ -diimine complexes as precursors of catalysts for olefin polymerization.





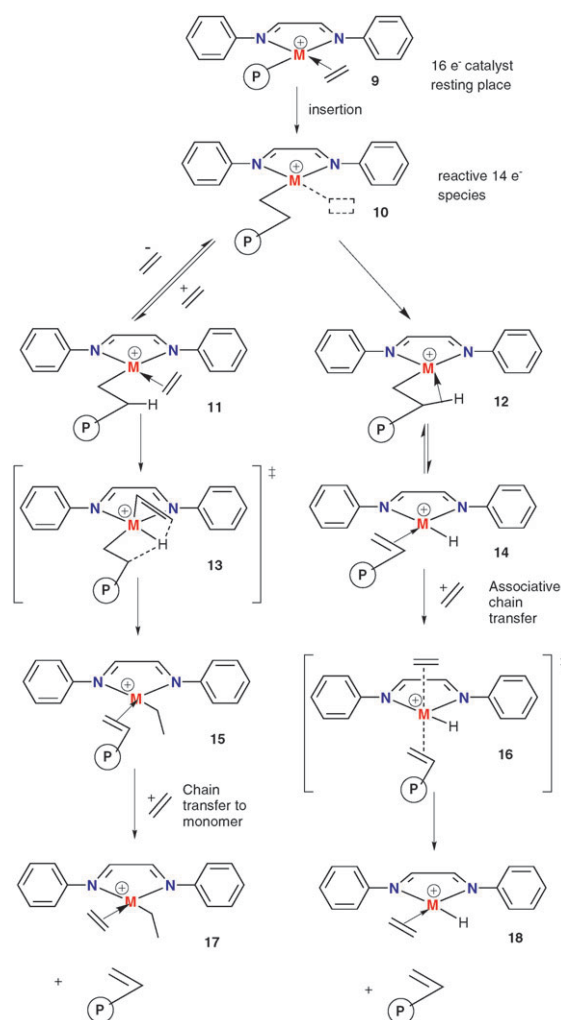
**Fig. 3** Axial (Ax) and equatorial (Eq) coordination sites of the  $\alpha$ -diimine metal center and their steric interaction with the bis-aryl *ortho* substituents.

bulky substituents on the  $\alpha$ -diimine ligand that are strategically blocking the axial sites of the metal center (Fig. 3).<sup>42</sup>

By design, the bis-aryl groups in the  $\alpha$ -diimine catalysts lie roughly perpendicular to the metal–diimine plane. As a result, the *ortho* substituents on the bis-aryl offer steric crowding at the axial sites of the metal center (Fig. 3). This steric crowding at the axial sites is critical for suppressing the associative chain transfer process. Brookhart's mechanistic studies have revealed that at the 16  $e^-$  catalyst resting state (**9**), both the growing polymer chain and the coordinated olefin occupy the two *cis*-equatorial sites of the active catalytic center (Scheme 1).<sup>54</sup>

Following migratory insertion of the bound olefin, the highly reactive 14  $e^-$  metal center **10** undergoes facile  $\beta$ -hydride elimination to generate an olefin hydride complex **14**. This intermediate is very susceptible to undergoing premature chain transfer through an associative ligand exchange with an incoming monomer from the axial position. In Brookhart's design, the bulky axial substituents of the catalysts effectively block the association of free olefin, thus retarding the rates of chain transfer and allowing the generation of high polymer. However, theoretical investigations by Ziegler<sup>55</sup> indicate that the olefin hydride intermediate is a transition state in the chain isomerization process. Thus a concerted chain transfer mechanism may be operating where hydrogen transfer occurs between the alkyl olefin resting state and the incoming monomer *via* the proposed intermediate **13**. Although experimental evidence has not been conclusive in distinguishing these possibilities, both of the proposed chain transfer processes are expected to proceed through the similar, 5-coordinate transition states **13** and **16** that should be disrupted substantially by the presence of ligand axial steric bulk. The bulky ligand environment increases the ground state energy of the catalyst resting state **9** or **11** so that the insertion barrier is lowered, leading to rapid insertion. Experimental results to date have not conclusively favored one mechanism over the other, but the Ziegler chain-transfer-to-monomer mechanism has been shown to apply for the Pd system.<sup>56</sup>

In the design of  $\alpha$ -diimine catalysts **7** and **8**, the *ortho* substituents on the bis-aryl  $\alpha$ -diimine catalysts offer steric crowding both above and below the metal center. Thus the steric bulk of the *ortho*-alkyl substituents has a significant impact on polymerization activity and polymer properties. In modifying the *ortho* substituents from methyl (**7c** and **8c**)



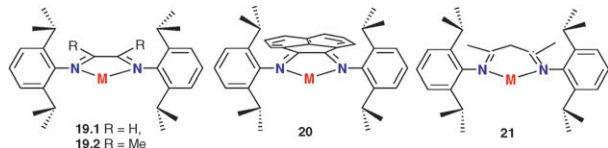
**Scheme 1** Mechanistic model of polymer growth and associative chain transfer on  $\alpha$ -diimine metal complex.

to iso-propyl groups (**7d** and **8d**), the complexes bearing more bulky isopropyl groups afford much higher molecular weight polymers at significantly higher polymerization activity than the corresponding methyl substituted complexes.

This is a very versatile system because the ligand can be easily varied. A large variety of structural permutations on the bis(aryl)- $\alpha$ -diimine basic motif have been reported from both academic and industrial laboratories.<sup>44</sup> Catalyst tuning has been achieved by modifying the backbone, sterics, electronics, and chirality of the  $\alpha$ -diimine ligand. As frequently seen, slight variation in the ligand can result in an enormous effect on the polymerization activity as well as the nature of the polymer products. In the following sections, we will survey some important examples of catalyst designs based on the  $\alpha$ -diimine ligand framework.

**3.1.1 Backbone effects on diimine ligand design.** The nature of the diimine backbone significantly impacts the polymerization activity and the polymer molecular weight. In changing the  $\alpha$ -diimine backbone from H to Me (**19.1**, **19.2** respectively), the Pd(II) complex showed dramatic improvement in catalyst activity and polymer molecular weight, while the Ni(II) catalyst showed an increase in polymer molecular weight

and branching density.<sup>42</sup> In comparison with the acenaphthyl (**20**)  $\alpha$ -diimine backbone, the Ni(II) complex having the methyl substituted ligand (**19.2**) gave higher molecular weight polymers and higher activity.<sup>42</sup> Thus, in terms of catalyst design, generally the methyl  $\alpha$ -diimine backbone is more effective in giving high MW PE and high activity. The acenaphthyl backbone, however, exhibits more stability at higher temperature.<sup>71</sup>

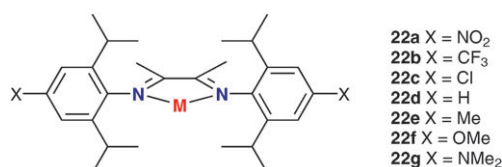


The observed impact of the diimine backbone can be explained from the X-ray crystal structure analysis of the Pd complex **19.2**.<sup>54</sup> The 5-membered Pd- $\alpha$ -diimine chelate ring shows a narrower N-Pd-N bite angle ( $74.81^\circ$ ) and an increased steric crowding in the metal coordination plane as well as in the axial site. This results from the steric repulsion of the methyl groups in the  $\alpha$ -diimine backbone, which forces the bis-aryl groups into a concave shape affecting the sterics in the metal center and brings the *ortho* isopropyl groups closer to each other, thus blocking the axial sites more effectively. The increased steric crowding in the active catalytic center and axial site leads to the production of higher molecular weight polymers. In contrast, the complex that uses ligand **20** gave lower MW polymers and lower activity, due to the acenaphthyl backbone holding the bis-aryl rings farther away from the metal center, reducing steric interaction. In ligand **21**, which is designed with a methylene spacer inserted in the diimine backbone, the  $\beta$ -diimine Ni(II) and Pd(II) complexes afforded much lower MW PE.<sup>57</sup> This is because the 6-membered metal-diimine chelate ring is puckered and the bis-aryl groups tilt away from perpendicular orientation relative to the metal-diimine plane, causing the iso-propyl substituents to steer away from the axial sites and leaving the metal center less sterically shielded.

### 3.1.2 Electronic effects on bis(aryl)- $\alpha$ -diimine ligand system.

An important parameter in catalyst design is the impact of ligand electronic effects on the catalytic activity. The electronic effects of  $\alpha$ -diimine ligands towards polymerization properties were examined recently in our laboratory.<sup>58,59</sup> Ligand electronics have been shown to play substantial roles in organometallic transformations.<sup>60</sup> In our study, we introduced a series of substituents on the *para*-aryl position of the  $\alpha$ -diimine ligands to perturb the metal electronics (Fig. 4).

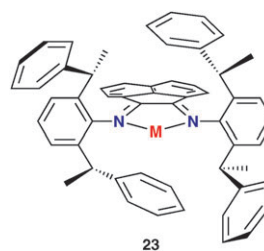
A range of electron donating and electron withdrawing substituents on the *para* positions of the bis-aryl ligand were prepared (Fig. 4). The systematic study reveals that the more strongly electron-donating ligand exerts significant stability



**Fig. 4** Substituent electronic effects on Ni(II) and Pd(II)  $\alpha$ -diimine catalysts.

and longer lifetimes on the Ni(II) and Pd(II) catalysts towards ethylene polymerization. It also showed that introduction of electron donating groups led to a dramatic increase in polymer molecular weight, *e.g.*, Pd(II) catalyst **22g** afforded polymer of more than twice the molecular weight compared to **22d**.<sup>59</sup> These effects are presumably due to the stabilization of the reactive, electron-deficient, and coordinatively unsaturated alkyl agostic intermediate. Ligands with electron-withdrawing groups, on the other hand, have short lifetimes and generally gave lower MW PE, presumably due to destabilization of the metal center increasing chain transfer rates. Moreover, the Pd(II) complexes bearing more electron-donating ligands showed high tolerance to polar comonomers and afforded copolymers with higher incorporation of the polar comonomers. Excitingly, the ligand electronic structure of the catalysts had a significant effect on the topology of the polyethylene formed: catalysts bearing more electron-withdrawing ligand afforded dendritic polymers.<sup>58</sup> The electronic structure of the catalyst system dramatically changed the relative rates of insertion and chain walking, thus affording the resulting polymer topology. This provides a fundamentally different approach in controlling polyolefin branching topology, complementing our previous strategy of controlling polymer topology *via* polymerization conditions.<sup>51</sup> Recently, the ligand electronic effects of remote substituents have also been demonstrated to dictate polyethylene microstructure and property (*vide supra*, Section 3.2, **47a-h**).<sup>61</sup>

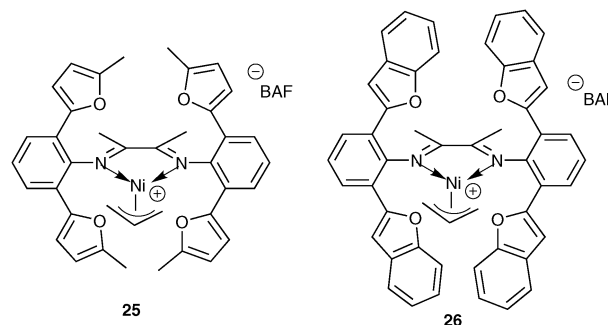
**3.1.3 Chiral  $\alpha$ -diimine ligand system.** Catalysts based on  $C_2$ -symmetric  $\alpha$ -diimine complexes have also been explored in the preparation of polyolefins with regio- and stereo-regularity. The typical  $\alpha$ -diimine catalysts undergo chain walking along the polymer backbone to produce branched polymers with no stereoregularity of the branches. The *trans*-2-butene polymerization using pre-catalysts **8c-e** showed regioregular methyl branches in every 3 carbons, but no stereocontrol was observed because these complexes are achiral.<sup>62</sup> To produce regioregular and stereocontrolled branches, Coates<sup>63</sup> and co-workers designed a chiral  $C_2$ -symmetric  $\alpha$ -diimine catalyst to control the chain walking in a more regular fashion. The Ni(II) catalyst **23** bearing chiral *sec*-phenethyl moieties in the *ortho*-aryl positions of  $\alpha$ -diimines provided high regio-regularity, comparable to **8c-e**, to the polymer produced from *trans*-2-butene: in every 3 carbons of the linear polymer, a methyl branch is formed. However, only the chiral ligand system imparts a high degree of isospecificity. In their proposed model, the two phenyl substituents in the axial direction  $\pi$ -stack with the acenaphthene backbone imparting a chiral pocket about the metal center resulting in a significantly enhanced enantiofacial selectivity.



**3.1.4 Teraryl substituted- $\alpha$ -diimine ligand design.** One crucial aspect of polymerization catalyst design is to ensure catalyst stability at the required polymerization conditions. For commercially viable processes, polymerizations need to be run at elevated temperature and often in the presence of a controlled amount of hydrogen gas for molecular weight control. One drawback of the Brookhart type  $\alpha$ -diimine catalyst is its rapid deactivation in the presence of hydrogen.<sup>64</sup> Interestingly, the catalyst reported by Rieger (**24**, Fig. 5) is stable in the presence of hydrogen.<sup>65</sup> Although the mechanism of H<sub>2</sub> stability is not clear, the use of phenyl groups instead of the alkyl groups on the *ortho* moieties of bis(aryl)- $\alpha$ -diimine suggests the critical role of more steric bulk in the axial direction.<sup>66</sup> Moreover, the axial blocking effect of the phenyl groups has a direct impact on the catalyst activity and degree of polymer branching. Due to the repulsive interactions in the 4-*tert*-butyl substituents in **24c** compared to the 3,5-dimethyl substituents in **24b**, a twisted geometry is observed in the former, resulting in more open space in the axial direction which the monomers can access for associative chain transfer to occur and providing space for the chain transfer to proceed *via* monomer exchange mechanism.<sup>55</sup> The twisted geometry of **24c** also affords a smaller cone volume in the metal coordination plane compared to **24b**, which prevents the formation of bulky polyolefin to give mostly linear polymer.<sup>67</sup> The system shows the impact of the *ortho*-phenyl substituents, which determines the axial blocking effect and cone-like space in front of the metal center, defining the polymer molecular weight and branching density.

A similar series of Ni(II) catalysts **25** and **26** bearing *ortho*-difuryl substituents instead of phenyl moieties has been designed by Ionkin and Marshall<sup>68</sup> based on the axial blocking

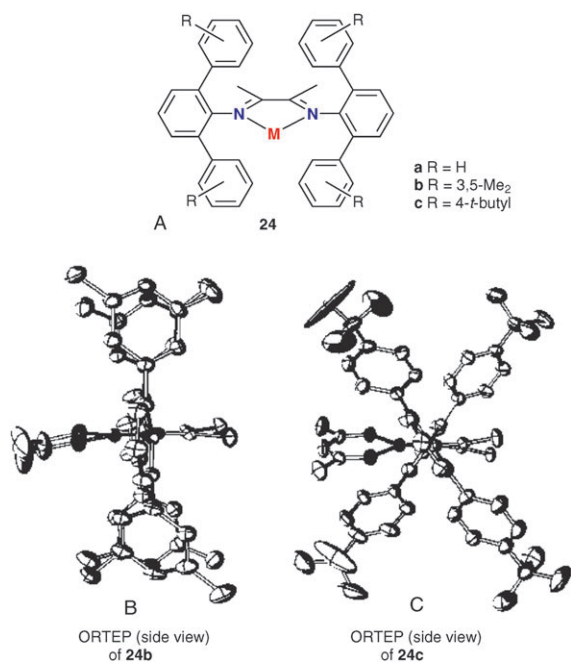
effect of the *ortho*-aryl substituents. These catalysts are noteworthy for their high thermal stability exhibiting good activity even at 150 °C. Although the polymers produced have broad polydispersity, the bulkier catalyst **26** performs better than **25** to afford high molecular weight polymers. The branching density of the resulting polymer, however, is still relatively low even under the high temperature conditions.



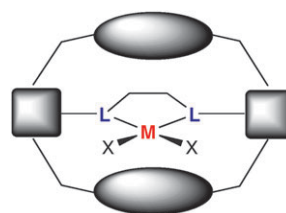
### 3.1.5 Catalyst design based on cyclophane $\alpha$ -diimine ligands.

The design of the  $\alpha$ -diimine-based late-metal polymerization catalysts is successful because the  $\alpha$ -diimine ligands provide appropriate steric and electronic effects to the metal center. A key aspect in the design is the steric bulk in the axial sites, which is critical for the catalytic activity and formation of high MW polymers. However, an inherent limitation of the  $\alpha$ -diimine system is that the axial blocking ability and the catalyst thermal stability suffer at elevated polymerization temperatures. This is due to the rotational flexibility of the ligand at elevated temperature, leading to dramatic reduction of polymer MW and catalyst deactivation due to C–H activation of the *ortho*-substituents.<sup>42,69</sup> To address these issues, our laboratory has designed a novel macrocyclic  $\alpha$ -diimine system. We envisioned that the closed cyclic design should fix the axial blocking groups in their positions, thus minimizing the ligand thermal motion and preventing the chain transfer from occurring and the catalyst from being deactivated (Fig. 6).

Our macrocyclic ligand design is built upon the fundamental understanding of various homogenous catalyst systems that have shown successful polymerization activities. The designs of these catalysts often share common features, *i.e.*, the choice of the ligand is dependent on its ability to donate appropriate electrons to the metal, form stable complex with the metal ion, and protect the active catalytic center. Moreover, the complex should be able to facilitate polymerization upon activation. This is generally observed for complexes whose active centers are located on two-*cis* coordination sites where one site is used for monomer entry and the other is for polymer growth.



**Fig. 5** (A) Molecular structures of teraryl  $\alpha$ -diimine catalyst; X-ray crystal structures of **24b** (B) and **24c** (C) [X-ray crystal structures reproduced with permission from ref. 67].



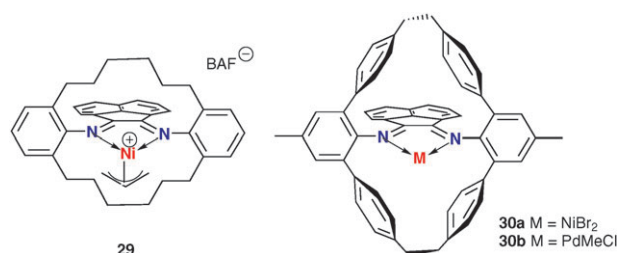
**Fig. 6** Design of cyclophane-based complexes.



Our general concept of cyclophane catalyst design is illustrated in Fig. 6, in which a macrocyclic framework is employed and the metal is strategically positioned at the core of the macrocyclic ligand.<sup>69,70</sup> The chelation of the metal is achieved by installing appropriate intra-annular binding sites that donate electrons to the metal and whose coordination geometry matches with the chosen metal to form a stable complex. The well-defined cavity and sterically hindered microenvironment of the macrocyclic framework will shield the metal center from axial directions, thus potentially protecting the catalytic center. Activation of the complex would open two-*cis* coordination sites in the metal, in which one site will accommodate the incoming monomer and the other site will hold the growing polymer chain. Moreover, we envisioned that due to the rigidity of the macrocyclic design, some possible detrimental side reactions and eventual catalyst deactivation may be prevented.

Specifically, we have designed a series of cyclophane-based  $\alpha$ -diimine ligands to address the high sensitivity of the regular  $\alpha$ -diimine catalyst at elevated temperature. The rapid decomposition of the acyclic  $\alpha$ -diimine complex **27** (Fig. 7) is attributed to the rotational flexibility of the aryl–nitrogen bond at elevated temperature. This bond rotation displaces the critical axial positions of the *ortho* isopropyl groups, resulting in open spaces which the ethylene monomer can readily access or where the process of chain-transfer-to-monomer can proceed.<sup>55</sup> Hence at conditions of elevated polymerization temperature, the ethylene associative chain transfer or chain-transfer-to-monomer processes increase, leading to a dramatic decrease in polymer molecular weight.<sup>71</sup> Moreover, at high temperature, the bond rotation will result in the aryl groups rotating away from their perpendicular position towards the coordination plane such that the *ortho* isopropyl groups approach proximity to the metal center for C–H activation to form metallacycles. This phenomenon, which was proposed as one potential deactivation pathway,<sup>54</sup> accounts for the low thermal stability of this class of catalyst. In our design of a cyclophane-based complex **28**, the macrocyclic ligand holds the metal center at its core and offers complete blocking of the axial coordination sites. Due to its rigid closed framework, the macrocyclic ligand prohibits free rotation of the aryl–nitrogen bonds, making the catalyst potentially capable of affording high MW polymers even at high temperature. The lack of

rotational flexibility likely eliminates the possible catalyst decomposition *via* C–H activation.



We have successfully prepared alkyl-bridged cyclophane complex **29** and aromatic cyclophane complexes **30a** and **30b**. Whereas the bulky and rigid structure offered by the alkane bridges in cyclic complex **29** fits the intended design concept described above, the alkyl-bridged cyclophane complex (**29**) gives disappointing performance in catalyzing ethylene polymerization.<sup>73</sup> A closer examination of the structure of complex **29** reveals that the excessive steric crowding of the alkyl bridges above and below the metal coordination plane may have inhibited the entry of ethylene monomer or may have increased the insertion barrier, resulting in low polymerization activity. The same observation has been noted for the half-cyclophane system.<sup>72</sup> X-Ray analysis of **29** revealed that some hydrogen atoms in the alkyl bridge are very close to the metal centers, which may also lead to C–H activation and further catalyst deactivation.<sup>73</sup> This process exemplifies the subtlety involved in designing a successful catalytic system: although axial steric bulkiness is critical for blocking chain transfer and increasing catalyst activity, excessive bulky axial moieties may disrupt monomer entry or totally inhibit the monomer coordination.

Our aromatic cyclophane-based macrocyclic complexes, **30a** and **30b**, turn out to be very successful catalysts.<sup>69</sup> The aromatic cyclophane ligand shares some similarity to Rieger's *m*-terphenyl-based ligand,<sup>65</sup> but a key new design strategy is to connect the *m*-terphenyl moieties by an ethylene bridge, forming a cyclophane. The X-ray structure and space filling model of the Pd(II) complex **30b** revealed effective axial shielding of the catalytic center by the cyclophane framework leaving two front *cis* coordination sites accessible for polymerization (Fig. 8). Moreover, the distances of the metal to any C–H bond in the ligand is remote for C–H bond activation to occur, thus the cyclophane ligand design should avoid this potential catalyst-deactivation pathway.

The Ni(II) catalyst **30a** exhibits high activity for ethylene polymerizations and affords high MW polymer even at elevated temperatures (e.g., polymerization condition at 90 °C: TOF =  $1.07 \times 10^6 \text{ h}^{-1}$ ;  $M_n \approx 300\,000 \text{ g mol}^{-1}$ ).<sup>69</sup> The catalyst is thermally stable at 90 °C, and no observable deactivation occurs below this temperature. This is in contrast to Brookhart's acyclic Ni(II)- $\alpha$ -diimine systems, for which MWs of PEs usually decrease rapidly with increasing temperature.<sup>42</sup> Moreover, the thermal stability and branching density is considerably higher than the similarly *m*-terphenyl-based acyclic system designed by Rieger<sup>65,67</sup> illustrating the importance of cyclophane geometry. We attribute this to the

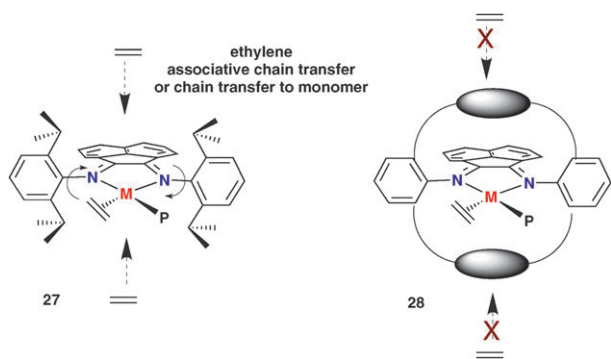
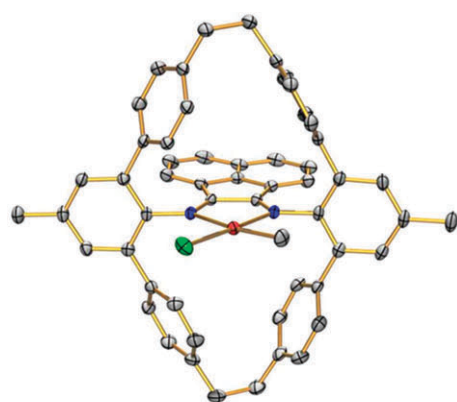
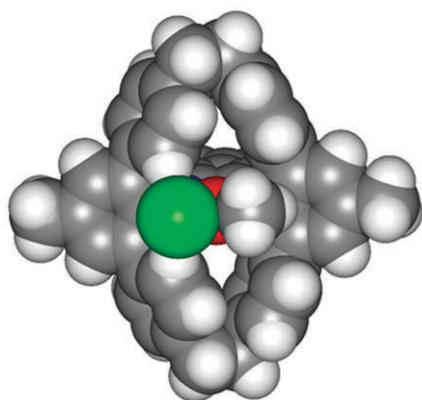


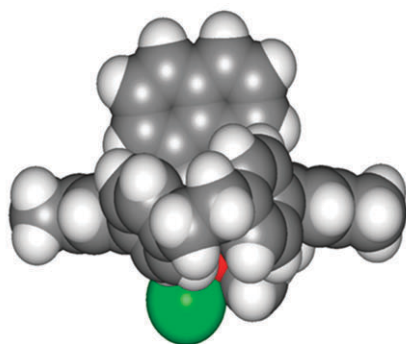
Fig. 7 Comparison of acyclic and cyclophane  $\alpha$ -diimine complexes.



ORTEP drawing



CPK model (front view)



CPK model (top view)

**Fig. 8** X-Ray crystal structure and space filling model of **30b** [Reproduced with permission from ref. 69].

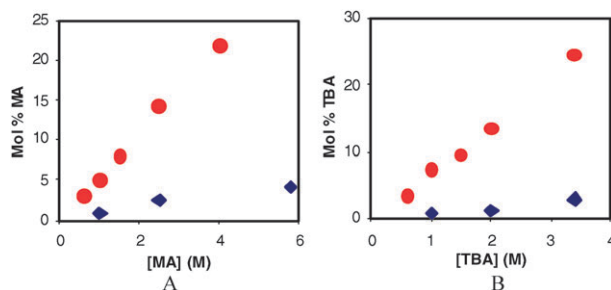
suppression of associative chain transfer or chain transfer to monomer processes by the bulky axial ligand and the absence of free rotation of aryl–N bonds by the rigid cyclophane framework.

The robustness of the cyclophane Ni(II) catalyst **30a** is further demonstrated by its ability to control the polymer molecular weight *via* living polymerization of  $\alpha$ -olefins.<sup>74</sup> Most active olefin polymerization catalysts usually lose living polymerization features at elevated temperatures and thus

living olefin polymerizations are generally conducted at subambient temperatures to suppress potential chain termination and chain transfer reactions.<sup>75</sup> Due to its unique cyclophane ligand framework, complex **30a** affords living polymerization of propylene and 1-hexene at temperatures up to 75 °C and gives polyolefins with well controlled MW, narrow molecular weight distribution (MWD) and unique microstructures,<sup>74</sup> differing significantly from products of the acyclic catalyst.<sup>76</sup> The living polymerization feature of the cyclophane catalyst at elevated temperature is attributed to the excellent protective effects of the cyclophane ligand environment. This system offers the possibility of developing preparations of various polyolefin architectures at more practical experimental conditions.

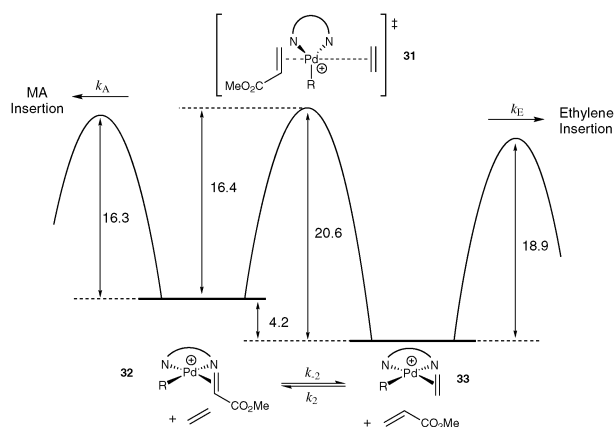
The Pd(II)–cyclophane  $\alpha$ -diimine catalyst **30b** was also investigated for ethylene homo- and co-polymerization. One major surprise for the Pd(II) system is that it is significantly more efficient for incorporating polar olefin in copolymerization with ethylene and polar comonomers like acrylates.<sup>77</sup> This is significant because there remains a scientific challenge in olefin polymerization catalysis to discover transition metal catalysts that can incorporate polar olefins efficiently. As shown in Fig. 9, the efficiency for incorporation of methyl acrylate (MA) and *tert*-butyl acrylate (TBA) into copolymers has been shown to increase significantly for our cyclophane catalyst **30b** as compared to the original acyclic catalyst (**7e**), even at low starting concentrations of acrylates.<sup>77</sup>

This interesting catalytic property of the Pd(II)–cyclophane catalyst is again due to the unique microenvironment of the cyclophane ligand. Our detailed mechanistic investigation using low temperature NMR studies has elucidated a unique mechanistic origin for the increased efficiency of polar olefin incorporation.<sup>78</sup> Fig. 10 shows the free energy diagram of the copolymerization of ethylene and MA for the cyclophane system. Contrary to the acyclic  $\alpha$ -diimine system, inspection of the free energy diagram indicates that the fast equilibrium of olefin exchange, a prerequisite for the Curtin–Hammett scenario, does not exist in the cyclophane system. The cyclophane catalyst has a significantly higher barrier for olefin exchange equilibrium (20.6 kcal mol<sup>−1</sup>) than the acyclic catalyst. This unusual phenomenon originates from the effective axial blocking effect of the cyclophane ligand, which offers a large barrier, hindering olefin substitution and equilibration. The higher activation energy is due to the steric bulkiness of



**Fig. 9** (A) Incorporation ratio of MA into copolymer *versus* MA concentration for catalysts **7e** and **30b**. (B) Incorporation ratio of TBA into copolymer *versus* TBA concentration for catalysts **7e** and **30b**. Red circle is for catalyst **30b** and blue diamond is for catalyst **7e**.



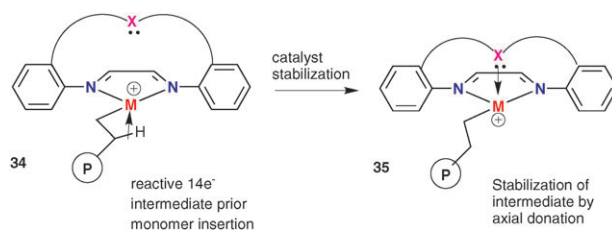


**Fig. 10** Free energy diagram of ethylene/MA copolymerization at 35 °C by the cyclophane catalyst. Energetic values are given in kcal mol<sup>-1</sup>. [Reproduced with permission from ref. 78].

the cyclophane ligand such that the proposed 5-coordinate transition state **31**, for both the associative ligand exchange or chain transfer to monomer models, is highly disfavored by the bulky cyclophane ligand framework. The barriers to MA insertion and displacement by ethylene for MA complex **32** are comparable ( $k_A/(k_{-2}[\text{C}_2\text{H}_4]) \approx 1.4$ ), indicating that a substantial amount of **32** will undergo MA insertion before displacement by ethylene. This effect suppresses the cyclophane catalyst's ability to discriminate between monomers (ethylene vs. polar olefin) for binding, thus giving rise to high polar comonomer incorporations. This effect clearly results from the cyclophane ligand environment, which is in sharp contrast to the acyclic  $\alpha$ -diimine catalyst.

The cyclophane based late-transition metal  $\alpha$ -diimine system developed in our laboratory represents a successful example of rational design of late-metal catalysts for olefin polymerization. The improvement in thermal stability and the enhanced efficiency of incorporating polar olefins for the cyclophane catalyst demonstrate the important role of the cyclophane ligand microenvironment on their catalytic properties.

**3.1.6 Axial donating  $\alpha$ -diimine ligands.** In another study, we demonstrated a different concept for catalyst design based on mechanistic understanding of the  $\alpha$ -diimine system. A key aspect of designing successful late-metal polymerization catalysts is to suppress chain transfer processes. In previous systems, this was accomplished by steric blocking of the axial sites of the active metal center in order to suppress the processes of associative chain transfer or chain transfer to monomer. In contrast, in a recent study, we designed a system that restrains chain transfer by making the axial site unavailable for side reactions *via* stabilization of the reactive catalyst intermediate. The general concept is based on stabilizing the most reactive 14 e<sup>-</sup> intermediate (Scheme 2). In Brookhart's mechanistic model of the  $\alpha$ -diimine system,<sup>54</sup> the most reactive intermediate (**34**) is a 14 e<sup>-</sup> cationic complex that contains the growing polymer chain. This reactive intermediate can have agostic interaction with the  $\beta$ -hydrogen and further undergo reversible  $\beta$ -hydride elimination, forming a square planar 16 e<sup>-</sup> olefin hydride intermediate. This olefin hydride complex

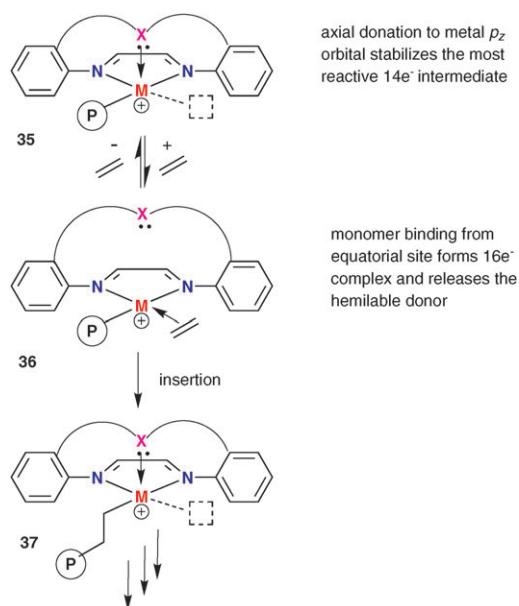


**Scheme 2** Catalyst stabilization model by axial hemilabile donor ligand.

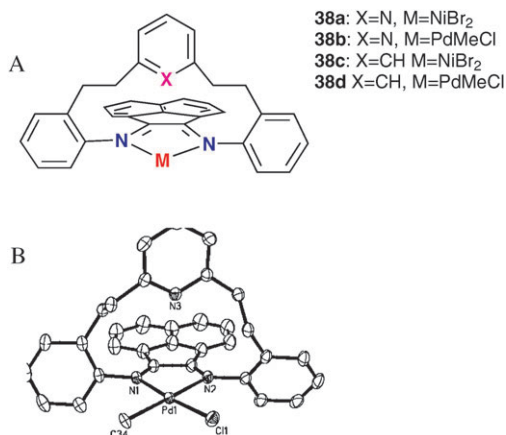
is highly susceptible to associative ligand exchange or chain transfer to monomer by coordination of a new olefin at the axial site, leading to premature chain termination.<sup>42,71,79</sup> Our design utilizes a tethered group that can stabilize the reactive intermediate *via* axial coordination with the metal (**35**). Stabilization of this intermediate shuts down the possible chain transfer processes and potential catalyst deactivation.

We thus envisioned a class of new catalysts whose design is based on a semi-cyclic system with an axial hemilabile ligand that reversibly interacts with the metal. We proposed that a hemilabile ligand can “temporarily protect” the most reactive 14 e<sup>-</sup> intermediate *via* axial donation and suppress potential side reactions such as chain transfer. Upon coordination of the next olefin, the hemilabile ligand should be able to release from the metal and allow the metal active site to proceed with next insertion (Scheme 3).

We hypothesized that to affect the facile reversible interaction with the metal, the hemilabile donor should be tethered in the ligand and positioned strategically in the axial orientation to allow interaction with the appropriate orbital (*i.e.*, empty  $p_z$ ) of the metal.<sup>80</sup> In contrast to the steric bulk concept in the other  $\alpha$ -diimine-based late-metal catalysts which require steric bulk at both the top and bottom axial faces, our new design leaves the bottom rim of the diimine–metal plane completely open. We proposed that stabilization of the reactive metal



**Scheme 3** Concept of hemilabile axial donor  $\alpha$ -diimine ligand.



**Fig. 11** (A) Chemical structure of hemilabile complexes; (B) X-ray crystal structure of **38b** [X-ray crystal structure reproduced from ref. 81].

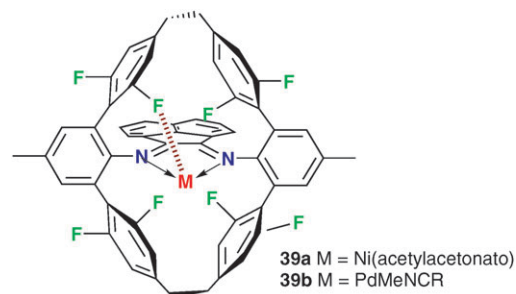
center from one axial side should suppress  $\beta$ -hydride elimination and hence, the subsequent associative chain transfer or chain transfer to monomer. To demonstrate this design strategy, a pyridine group, whose lone electron pairs can act as electron donor to the metal, is tethered to an  $\alpha$ -diimine ligand. We thus prepared the complexes **38a** and **38b** (Fig. 11). For comparison, a control system (**38c** and **38d**) having the same sterics and geometry but without the nitrogen donor was likewise prepared.<sup>81</sup>

In complex **38b**, the pyridine nitrogen is beyond bonding distance to the metal (N–Pd = 3.814 Å) in solid state crystal form. However, as revealed in <sup>1</sup>H NMR analysis, the pyridine tether linkage exhibits flexibility indicating facile forward and backward swinging of the pyridine into different conformers.<sup>81</sup> The activation energy for the exchange of the two conformers is estimated to be  $\sim 12.5$  kcal mol<sup>−1</sup>. This conformational flexibility may provide a mechanism for the hemilabile axial donation of the pyridine to the metal. Indeed, the pyridine in the complex has been shown to play an active role in inhibiting chain transfer and to produce high molecular weight PE. Activation of complex **38a** with AlMe<sub>2</sub>Cl results in a highly active catalyst for ethylene polymerization at 35 °C with a TOF of 60 000 per hour (16 800 kg PE/(mol Ni·h)). It also affords significant changes in the polymer microstructures, yielding high molecular weight linear polymer ( $M_n$  = 56 460 g mol<sup>−1</sup>, PDI = 2.2, at 200 psi ethylene and 35 °C;  $T_m$  > 130 °C). The  $T_m$  data indicate a polyethylene that is highly linear and crystalline.<sup>81</sup> Despite the open site in the bottom rim of the complex, the formation of high molecular weight PE supports our initial hypothesis on metal stabilization in preventing chain transfer. This contrasts to the very short oligomers produced from regular  $\alpha$ -diimine systems with no or mono *ortho*-substituents on the anilines.<sup>71</sup>

In a direct comparative study between hemilabile pyridine complex **38a** versus the complex containing nondonating phenyl tether **38c**, the latter affords very low molecular weight and broad polydispersity ( $M_n$  = 6900 g mol<sup>−1</sup>, PDI = 5.6, at 200 psi ethylene and 35 °C,  $T_m$  = 122 °C). This result demonstrates the importance of the axial donating group in regulating catalyst properties.

The Pd(II) catalyst **38b** showed a more pronounced difference compared to the control system **38d**. In the presence of NaBAR<sub>4</sub> and excess AlMe<sub>2</sub>Cl, complex **38b** resulted in high activity, giving high molecular weight linear PE with high crystallinity ( $M_n$  = 880 000 g mol<sup>−1</sup>, PDI = 1.9, at 1 atm of ethylene and 25 °C;  $T_m$  = 134 °C; branching density = 5.1 branches per 1000 C). In sharp contrast, the control complex **38d** only produced short oligomers with high branching density ( $M_n$   $\approx$  1000 g mol<sup>−1</sup>, PDI = 1.5, at 1 atm of ethylene and 25 °C;  $T_m$  = n/a; branching density: 104 branches per 1000 C). These results illustrate that the axial pyridine nitrogen together with AlMe<sub>2</sub>Cl play a very critical role. The peculiar role of the activator suggests the subtlety of precise mechanism for this system.

Although the exact mechanism is still under investigation, the designed catalyst based on axial coordination effectively suppresses  $\beta$ -hydride elimination and chain transfer processes, resulting in the production of high molecular weight polymers with linear crystalline structure, thus extending the arsenal of catalytic systems that can produce specialized polymer in a controlled manner.



In another design, we combine the rigid framework of the cyclophane ligand and the interacting capability of an axial ligand with the metal center. Specifically, the *ortho*-hydrogens on the *ortho*-phenyl groups in our original cyclophane- $\alpha$ -diimine ligand are strategically replaced with fluorine atoms (**39a** and **39b**).<sup>82</sup> We envisioned that the axially-oriented fluorine atoms can interact with the metal center through their lone pair of electrons, which provides additional stabilization to the reactive species. Indeed, substitution of fluorine atoms resulted in significant changes to the polymerization behavior for these catalysts. Compared to ordinary cyclophane systems, the fluorinated cyclophane catalysts afforded higher molecular weight polymers with lower branching density and exhibited further enhanced thermal stability (**39a**). NMR studies have confirmed direct interactions between fluorine atoms and the active metal center.<sup>82</sup>

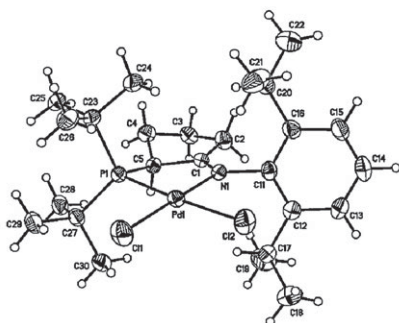
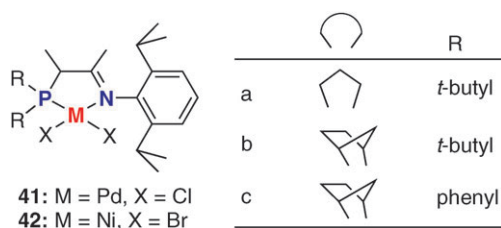
**3.1.7 Fe(II) and Co(II) tridentate complexes.** Complexes of Fe and Co with tridentate bis(imino)pyridine ligands<sup>83</sup> **40**, independently developed by Bennett,<sup>84</sup> Brookhart,<sup>43,85</sup> and Gibson,<sup>86</sup> exhibit high performance for ethylene polymerization.<sup>87</sup> The catalysts have very high catalytic activity enabling the formation of highly linear polyethylenes. The bulkiness of the arylimino groups of the ligand can be manipulated such that either polymerization or oligomerization can be obtained. In general, the presence of two bulky substituents in the

*ortho* positions for both the aryl ligand rings in **40** affords high molecular weight PE, while oligomers are formed when these bulky substituents are absent. On the other hand,  $\alpha$ -olefins are formed if only one substituent is present on the aryl groups. The effect of the bulky substituents, as suggested by Ziegler's theoretical investigations on  $\alpha$ -diimine catalysts, also holds true in this tridentate system: bulky substituents destabilize the catalyst resting state such that the activation barrier for the chain transfer process increases, and thus long chain polymers are produced.<sup>55</sup>

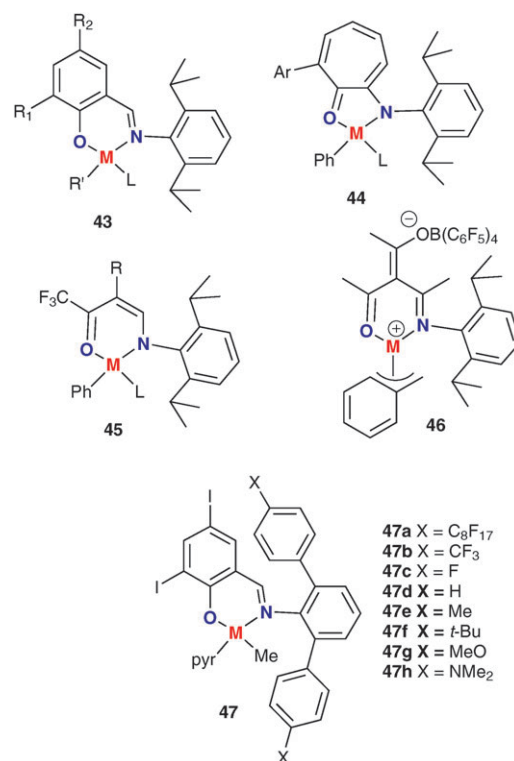


### 3.2 Design of catalyst based on chelating P<sup>+</sup>N, N<sup>+</sup>O, P<sup>+</sup>O ligands

A variety of late-metal polymerization catalysts have been designed in the last decade that utilize various chelating ligands. In our early catalyst studies, we designed a class of Pd(II) and Ni(II) catalysts based on phosphine imine (P<sup>+</sup>N) **41–42** (Fig. 12) in lieu of the classic diimine (N<sup>+</sup>N) system. Our rationale was that replacement of one imine site in the bis(imine) ligands with the better  $\sigma$ -donating phosphine may increase the binding strength of the ligand to the metal center and may impart thermal stability on the Ni(II) and Pd(II) complexes. Indeed, the (P<sup>+</sup>N)–Ni complex **42b** (M = Ni, L = Br, R = *tert*-butyl) exhibits significantly more thermal stability than the standard  $\alpha$ -diimine system, albeit at lower activity.<sup>88</sup> Although low MW PEs were produced, these are highly branched, exhibiting even branch-on-branches structure.



**Fig. 12** Catalysts containing [P<sup>+</sup>N] chelating ligands [X-ray crystal structure reproduced from ref. 88].



**Fig. 13** Representative features of catalysts based on [N<sup>+</sup>O] chelating ligands.

An interesting catalyst system designed by Grubbs *et al.*<sup>89</sup> is a series of the phenoxyimine–late-metal complexes **43** (Fig. 13). These complexes utilized the “harder” nitrogen based ligand by replacing of the P<sup>+</sup>O chelate in the neutral SHOP system into an N<sup>+</sup>O system. The oligomerization/polymerization activity of this class of catalysts is generally affected by steric and electronic properties of the salicylaldimine framework as well as the nature of the L ligand. For example, the Ni complex with phenoxyimine ligands (**43**, R<sub>1</sub> = 9-anthryl, R<sub>2</sub> = H, R' = Ph, L = PPh<sub>3</sub>) promotes ethylene polymerization to afford linear and low branched PE with MW  $\approx$  250 000. The bulky 2,6-diisopropyl phenyl group in **43**, despite its remote location relative to the Ni center, plays a crucial role as it affects the degree of branching and molecular weight of the polymer product.<sup>90</sup> It is interesting to note that these Ni complexes are highly tolerant toward polar functional groups, such that polymerization of ethylene in water<sup>91</sup> and in supercritical CO<sub>2</sub><sup>92</sup> has been demonstrated. Whereas the Ni complexes can copolymerize ethylene with functionalized norbornene, few reports of phosphine-based Ni catalysts for copolymerization with commercially relevant polar olefins such as acrylates are available.<sup>93</sup>

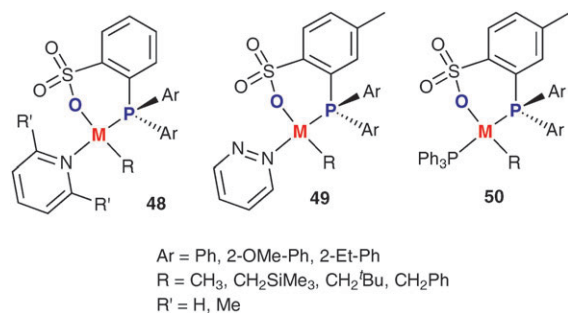
Brookhart and coworkers designed N<sup>+</sup>O based Ni system **44** using anilinoenone as ligands, which promotes ethylene polymerization and produces polymers with a wide range of branching density that depends on changes in pressure and temperature.<sup>94</sup> High catalytic activity was reported for complexes having anilinoenone ligands with remote CF<sub>3</sub> groups **45** (M = Ni; L = PPh<sub>3</sub>; R = COCF<sub>3</sub>). Upon activation, this complex exhibits high stability over long period and produces moderately-branched PE.<sup>95</sup> The



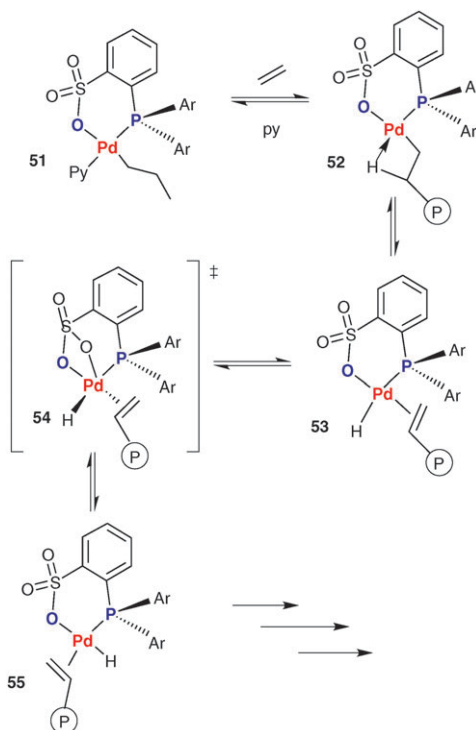
zwitterionic catalyst **46**, based on the  $\alpha$ -iminocarboxamide framework, yields branched polyethylene.<sup>96</sup> A series of Ni complexes (**47a–h**) designed with varying electron withdrawing and donating substituents positioned remotely from the active metal center were studied.<sup>61</sup> The ligand electronic effects of remote substituents were shown to influence the polymer microstructure, ranging from linear semicrystalline to highly branched amorphous PE. The excellent control of polymer microstructure is attributed to the remote substituents dictating the catalytic activity based on purely electronic effects.

A promising catalyst system that has attracted much attention recently is a series of Pd and Ni complexes based on phosphine–sulfonate ligands **48–50** (Fig. 14). Drent and Pugh *et al.* initially observed that polar comonomers are randomly incorporated into linear polyethylene catalyzed by a Pd complex of di(2-methoxyphenyl)phosphinobenzene-2-sulfonic acid.<sup>97</sup> The *in situ* generated active species in their study was believed to be  $[P^+O]PdR$  where  $[P^+O]$  is a generic phosphine–sulfonate ligand. The chain-walking processes in these  $[P^+O]PdR$  catalysts are much slower than chain growth, thus affording linear copolymers, which is in contrast to the facile chain-walking scheme for the  $\alpha$ -diimine–Pd catalysts. Theoretical studies indicate that the barrier to  $\beta$ -H elimination is indeed higher for  $[P^+O]PdR$  species than for  $(R\text{-diimine})\text{-Pd}(R)^+$  species.<sup>98</sup> On the contrary, occurrence of chain walking *via* repetitive  $\beta$ -hydride elimination and reinsertion of the olefin was suggested by Jordan *et al.*<sup>99</sup> and Claverie *et al.*<sup>100</sup> The direct participation of the sulfonate ligand is indicated in the experimental and theoretical study by Nozaki *et al.*<sup>101</sup> A unique *cis/trans* isomerization process was proposed for the Pd phosphinesulfonate system from **53** to **55**, *via* the so-called “Berry’s pseudorotation” (Scheme 4). The second oxygen atom of the sulfonate group (**54**) is proposed to be involved in the isomerization process as the associative ligand, which is one of the most unique features of the sulfonate group. The formation of the *cis* and *trans* PdH(alkene)(phosphine–sulfonate) complexes are readily observable in the presence of excess amounts of ethylene, leading to the production of linear polyethylene with high molecular weight. Thus, the olefin insertion dominates over  $\beta$ -hydride elimination in the presence of ethylene pressure while  $\beta$ -hydride elimination proceeds when ethylene is low.

The catalyst also enabled copolymerization of ethylene with CO to afford nonalternating copolymers.<sup>102</sup> Since the initial report by Drent and Pugh, a series of studies have been



**Fig. 14** Representative features of catalysts based on  $[P^+O]$  chelating ligands.



**Scheme 4** Proposed *cis/trans* isomerisation of the Pd phosphine-sulfonate system.<sup>101</sup>

reported on the copolymerization of ethylene with various polar olefins using more well-defined analogs of the Drent's catalyst.<sup>103</sup> Polar olefins like vinyl acetate,<sup>104</sup> acrylates,<sup>105</sup> acrylonitrile,<sup>106</sup> vinyl ether,<sup>107</sup> vinyl fluoride,<sup>108</sup> *N*-vinylpyrrolidinone and acrylamide<sup>109</sup> have been copolymerized with ethylene into the linear polyethylene backbone using phosphine–sulfonate Pd catalysts. Recently, Pd–phosphine sulfonate systems containing pyridine, lutidine or dihydrodicyclopentadienyl have been explored. These systems were shown to be effective for copolymerization of ethylene with acrylate and/or non-alternating copolymerization of ethylene and CO.<sup>109</sup>

These representative examples demonstrate that, in addition to  $\alpha$ -diimine ligands, other chelating ligands, including  $[N^+O]$ ,  $[P^+O]$  and  $[N^+P]$ , can form late-metal complexes as active catalysts for olefin homo- and copolymerization. This opens further possibility for new ligand design in developing novel catalysts for olefin polymerization. The Pd(II) phosphine–sulfonate complexes are particularly interesting because of their capability for copolymerization with a broad range of polar olefins.

#### 4. Conclusion

Based on environmental, energy, and cost effectiveness considerations, there is a huge driving force for the polymer industry to develop new catalytic polymerization reactions that can convert cheap and abundant monomers into novel materials at high efficiency and atom economy. Given the importance of olefin copolymerization with polar olefins, the research focus in the polyolefin catalysis field has been shifted

from early- to late-transition metal systems because late-metal systems have much better tolerance toward functional polar monomers. As surveyed in this article, the [N<sup>+</sup>N]  $\alpha$ -diimine-based late-metal system is particularly versatile, allowing for fine-tuning the ligand structure to control the catalytic properties. Among further studies of the  $\alpha$ -diimine-based late-metal system, a notable development is the design of rigid cyclophane-based catalysts<sup>70</sup> that offer significantly improved catalyst thermal stability,<sup>69</sup> living polymerization at elevated temperatures,<sup>74</sup> and efficient incorporation of polar comonomers for copolymerization.<sup>77,78</sup> In addition to  $\alpha$ -diimine-based systems, significant progress has been made in the design of various other chelating ligands based on [N<sup>+</sup>O], [P<sup>+</sup>O] and [N<sup>+</sup>P] motifs for late-metal polymerization catalysts. A promising system among this family is a series of Pd-phosphine-sulfonate complexes.<sup>97</sup> These catalysts are especially exciting because of their ability to copolymerize ethylene with a number of commercially relevant polar comonomers.<sup>103</sup>

The examples highlighted in this review showcase the power of catalyst design for controlling olefin polymerization. We believe there is tremendous potential for further design and development of new catalytic systems that can efficiently convert common olefin feedstock into high value polymeric materials with designer compositions, functionalities, and polymer architectures. Toward this goal, parallel efforts are needed for “new catalyst design through combined experimental, mechanistic understanding, and improved computational modeling of catalytic processes” for further advancement of this field.<sup>3</sup>

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