

Review

Recent advances on α -diimine Ni and Pd complexes for catalyzed ethylene (Co)polymerization: A comprehensive review

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ABSTRACT

α -Diimine Ni and Pd complexes are one of the most examined late-transition organometallics in the application of catalyzed ethylene (co)polymerization. These organometallic catalysts provide unique advantages and particular opportunities to tailor the architectures, composition, and topology of synthesized polymers through catalyzed polymerization. Two decades after their initial discovery, they are still drawing extensive attention in both academia and industry. More recently, researchers have studied the effect of structural modifications on the α -diimine Ni and Pd complexes and their catalytic behaviors in ethylene (co)polymerization. This review highlights the recent progress in the developments of α -diimine Ni and Pd complexes achieved in the last decade. The chain-walking mechanism as a unique catalytic behavior of α -diimine Ni and Pd complexes is also addressed. The versatile synthesis of ligands and complexes enables researchers to tailor the catalytic performance and the microstructures of polyethylene. Correlations between their structural tunes and catalytic behaviors, polymer properties, and the ethylene copolymerization with polar monomers are comparatively presented and discussed. The heterogenization study of α -diimine Ni and Pd complexes on a solid support for heterogeneous catalysis is also comprehensively summarized. The review is broadly classified into four sections which includes i) the coordination-insertion chemistry in ethylene (co)polymerization, ii) the modification of ligand structure, iii) their application in the field of heterogeneous polymerization, iv) and the properties of the synthesized polymers, followed by the short summary and outlook for their potential studies and applications.

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Contents

1. Introduction	2
2. Coordination-insertion chemistry	3
2.1. Chain-walking mechanism for ethylene polymerization	3
2.2. Copolymerization with polar monomer	4
3. Recent developments in modified α -diimine Ni and Pd complexes	6
3.1. N-aryl modification	7
3.2. Backbone modification	15
3.3. Binuclear complexes	18
3.4. Functional group modification	20
4. Heterogeneous polymerization	23
5. Polymer properties	26
6. Conclusion and outlook	28
Declaration of Competing Interest	28

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Acknowledgment	28
References	28

1. Introduction

At present, >300 different grades of polyolefins are commercially available for different applications. Particularly, polyethylenes (PE) and polypropylenes (PP) are the most important materials produced by the petrochemical industry [1]. Together, they account for the largest segment of commercial polymeric materials [2]. Thanks to the dramatic developments in catalyzed polymerizations, the annual production of polyethylenes exceed 170 million tons, which is roughly 50 % of the global plastics production [3]. Although faced with environmental concerns, their superior mechanical performance still provides substantial advantages over their bio-based alternatives [4]. Coordination-insertion polymerizations catalyzed by transition-metal complexes are the predominant solutions for synthesizing polyethylenes on the industrial scale [5]. As already mentioned above, the major advantage of coordination-insertion chemistry is the outstanding control over polymeric microstructure, which also determines the macromolecular characteristics of polymers, such as the mechanical, thermal, and optical properties, and thus their final commercial values [6,7]. Consequently, the improvement of the catalytic per-

formance of organometallic catalysts in ethylene (co)polymerization is a key driving force in catalyst research.

Over fifty years ago, Ziegler and Natta won the Nobel Prize in Chemistry for their discovery of heterogeneous catalysts applied to olefin polymerizations [8,9]. Since then, the research field of transition-metal catalyzed olefin polymerization has seen great progress [10]. Compared to their early-transition metal rivals, the late-transition metal organometallics have been a topic of interest, because of their low oxophilicity, as well as their great potential in producing polymers containing various types of branches and polar functional groups [11–13]. Currently, a variety of structurally related late-transition metal organometallics have been applied in the ethylene (co)polymerization which includes α -diimine (N^N), phosphine (P^O), phenoxyimine (N^O) and pyridinylimine (N^N) types of catalysts (Fig. 1) [14–20]. Disparate catalytic performance and varying polymeric properties can be obtained via the utilization of different metal complexes. For example, phosphine-containing palladium catalysts have emerged as powerful alternatives for copolymerization of ethylene with polar monomers, leading to linear polymers [21–24]. However, the α -diimine Ni and Pd complexes still have a lot of advantages over the rest, including the

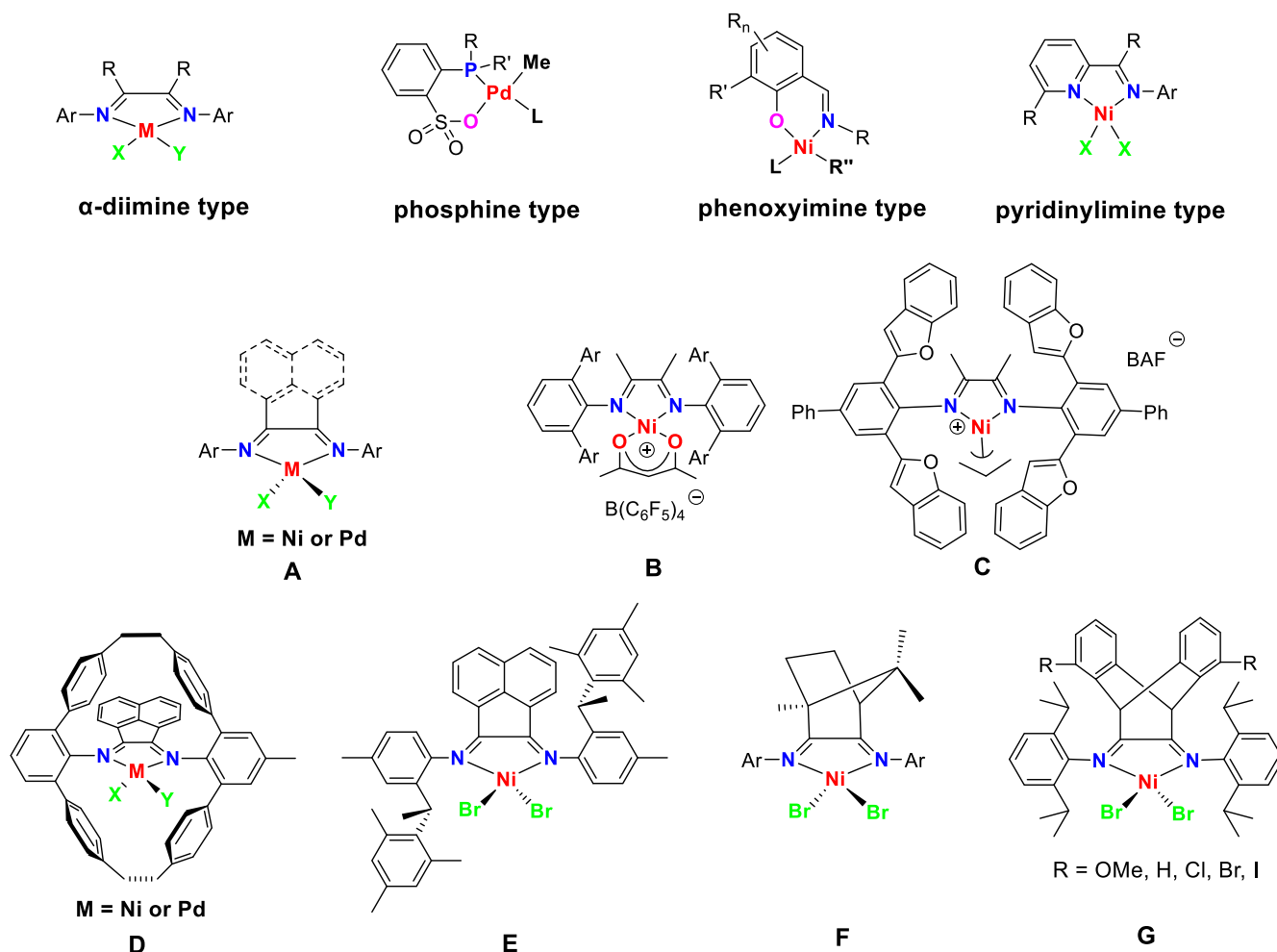


Fig. 1. Previously reported α -diimine Ni(II) and Pd(II) catalysts bearing various *N*-aryl substituents and backbones.

ease of synthesis and structural modification of ligands. In addition, late-transition metal complexes have attracted more considerable attention with the report of the highly active α -diimine Ni and Pd complexes by Brookhart (Fig. 1, A), for application in ethylene polymerization [25–28]. The branching density and topology of polyethylenes could be predictably adjusted by modifying the ligand structure and polymerization conditions. Thus elastic polymers could be synthesized using ethylene as a single monomer [29].

According to the previous studies, it was observed that small changes in the ligand structure entail significant variations in the macroscopic properties of the resulting polyethylenes [30]. *N*-aryl steric effects (Fig. 1. B, C, D, and E), backbone effects (Fig. 1. F and G), and remote substituent effects (Fig. 1. B and G) have been considered as main variables, influencing the catalytic behavior of α -diimine Ni(II) and Pd(II) complexes and consequently modifying polymer properties [31–39]. It is worth noting that the incorporation of phenyl groups on the *ortho*-moieties of *N*-aryl has helped achieve the control over the synthesis of either linear or branched polyethylenes, exhibiting ultrahigh molecular weight (up to 4×10^6 g mol⁻¹). These complexes were stable in the presence of hydrogen during ethylene polymerization (Fig. 1. B) [31]. Recent research activities in α -diimine Ni and Pd catalysts are mainly devoted to the modification of complex structures to achieve more efficient and higher degree of catalytic properties in homogenous (co)polymerization. Along these lines, unique and functional polymers, such as ultra-high-molecular-weight polyethylenes, elastomeric polymers, and highly branched and high-molecular-weight polyethylenes, have been reported through the elaborated designs of α -diimine Ni and Pd catalysts in catalyzed ethylene (co)polymerization [5].

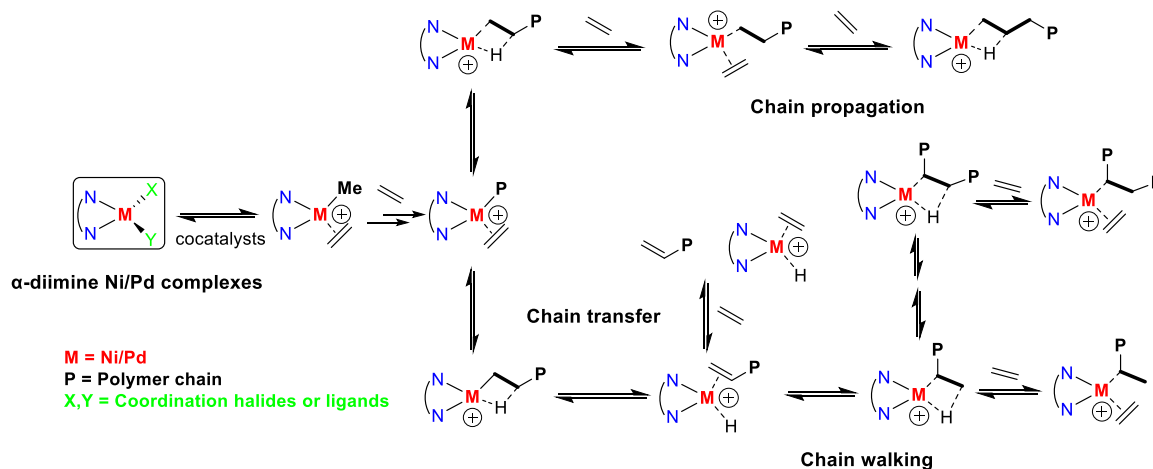
Over the last few years, several high-quality reviews on Ni and Pd complexes have been published, which partially includes the α -diimine Ni and Pd complexes for ethylene or α -olefin (co)polymerizations [5,11,30,40–47]. However, we still see the obvious gap between the published literatures and the specifically state-of-art discussion (especially fastened in the last decade). The lack of a comprehensive overview of α -diimine Ni and Pd complexes still remains, which includes the catalytic mechanisms, catalytic behaviors, and heterogeneous catalysis applications. Hence, this review emphasizes the structural variation of α -diimine Ni and Pd complexes, their catalytic performance during ethylene (co) polymerization, catalytic mechanisms in the ethylene polymerization and copolymerization with polar monomers, and the resulting polymer properties. Although researchers have invested extensive

efforts in the modifications of ligands and complexes structures, the discovery of promising catalytic systems is inevitably accompanied by trial and error. The relationship between structural variations (steric and electronic effects) of α -diimine Ni and Pd complexes and their catalytic performance is of great importance and thus need to be addressed in detail. More importantly for future application, the use of heterogeneous catalysts in the gas- and slurry-phase polymerization currently represents the predominant route in the industry [48]. Studies related to the immobilization of α -diimine Ni and Pd complexes onto solid substrates are a crucial step for their successful commercialization. This review has four main sections: i.e. i) Coordination-insertion chemistry; ii) Relationship between structural details and catalytic performance, iii) heterogeneous polymerization using supported α -diimine Ni and Pd complexes, iv) the mechanical properties and hydrophilicity of the produced polymers.

2. Coordination-insertion chemistry

2.1. Chain-walking mechanism for ethylene polymerization

Thermoplastic elastomers (TPEs) are rubber-like materials, which offer the ease of processing, recyclability, and enhanced mechanical characteristics. Their annual production is driven by industrial and consumer demands [49]. For TPEs synthesis, Dow's constrained geometry catalysts (CGC) were widely applied to produce the long-chain branches, which involve the incorporation of ethylene and higher α -olefin monomers. Short-chain branches in TPEs are achieved via copolymerization between ethylene and α -olefin monomer, catalyzed by transition-metal-based complexes. In contrast, α -diimine Ni and Pd complexes exhibit unique catalytic behaviors, producing high molecular weight polyethylenes with highly branched structures through the so-called chain-walking mechanism. This facile synthetic approach enables control of polyethylenes microstructures (either linear or branched polymers), solely using ethylene as the monomeric feed. The ethylene (co)polymerization catalyzed by the α -diimine Ni and Pd complexes provides a cost-effective alternative to more complicated and multi-step approaches to synthesize elastomeric materials, as it requires only a single step for their manufacturing [44]. A notable report describing the chain-walking mechanism was originally put forward by Fink et al. [50,51]. Soon afterward, Brookhart et al. refined this mechanistic method, which was then validated by both experimental and theoretical research [25,26,52,53]. Scheme 1



Scheme 1. Chain-walking mechanism in ethylene polymerization using α -diimine Ni and Pd catalysts.

illustrates the concept of the chain-walking mechanism for ethylene polymerization. Initiated by a cocatalyst, the chain-walking mechanism could be divided into several parts, namely chain propagation, chain transfer, and chain walking or isomerization. Cationic alkyl-metal active species provide superior activities. Hydrogen elimination and chain transfer lead to the formation of highly branched polyethylenes (Scheme 1). The catalytic metal center migrates along the polyethylene backbone via rapid β -H elimination and reinsertion as a chain-walking process [46]. The molecular weight of the obtained polyethylenes depends on the competition between the monomer insertion (chain growth) and the β -H elimination (chain transfer), where the latter process, followed by the reinsertion, leads to the formation of branched structures. More recently, Pei *et al.* have proposed a unique and new mechanistic model for the formation of long-chain-branches (LCBs), based on the classic chain-walking process catalyzed by α -diimine Ni complexes. The methyl branch was produced by a one-step chain walking followed by ethylene insertion. Consequently, the long-chain branching (LCBs) was directly obtained by ethylene insertion into the primary Ni-alkyl species, which is originally formed from the migration of the catalytic Ni center to the methyl terminal. Steric interactions from the *ortho*-aryl substituted anilines play a central role to limit the ethylene insertion to selectively generate the primary Ni-alkyl species and/or the secondary Ni-alkyl species with the α -methyl substituent. The proposed mechanism could explain the existence of methyl and LCBs without the formation of other short branches during the ethylene polymerization [54]. The bulky substituents on the *ortho*-N-aryl offer a steric crowding at the axial sites of the catalytic metal centers, which are perpendicular to the metal-diimine plane. This steric hindrance suppresses the associative chain transfer process. Such metal complexes bearing more bulky groups can lead to higher molecular weight polymers. Additionally, the diimine backbone influences the polymerization activity as well as the polymer molecular weight. The backbones with alkyl substituents are reported to yield higher molecular weight of polymers with narrower PDI than the planar acenaphthyl backbones [30]. Meanwhile, the steric enhancement on the diimine backbones significantly improves the thermal stability of the catalyst during ethylene polymerization. Side-arm effects (electronic

effects and weak interactions) from the remote substituents of the ligands similarly influence the catalytic activity and ensuing polymer properties.

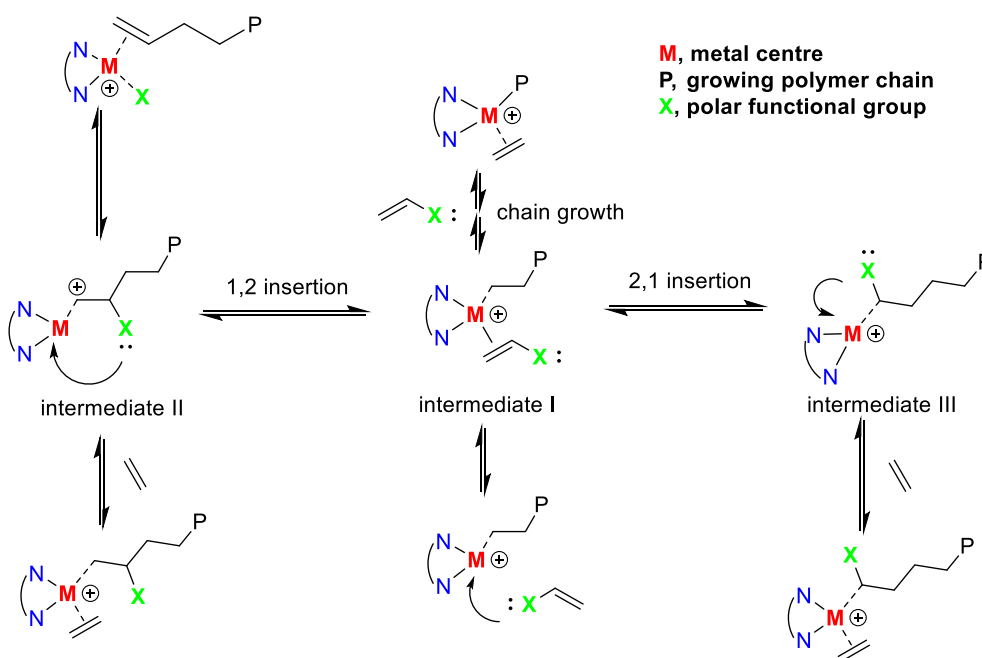
Generally, the polymerization temperature and ethylene pressure have a significant impact on the catalytic performance of the α -diimine Ni and Pd complexes. The high temperature increases the rotation of the C-Naryl bond, reducing steric hindrance at axial sites. Furthermore, a high rate of chain transfer is expected at high polymerization temperature, which leads to an increased reinsertion rate and the formation of branching. As the ethylene pressure is increased, chain propagation is preferred over chain transfer, therefore more linear and less branched polymers are formed. In addition, the α -diimine Pd complexes tend to undergo the chain-walking process, as compared to the corresponding Ni complexes.

Hyperbranched and amorphous polyethylenes can be produced via the α -diimine Pd catalyzed ethylene polymerization, while the α -diimine Ni complexes can produce mainly linear (few short-branches) polyethylenes with a well-defined melting point [25].

Due to this unique catalytic behavior of α -diimine Ni and Pd complexes, alkyl chains, such as methyl, ethyl, propyl, butyl, and even longer branches could be generated in the polymer backbones. Various polymers with elastic, semi-crystalline, and amorphous properties could be modulated with controlled chain-walking polymerization, using different reaction conditions and /or specially-synthesized Ni and Pd catalysts [42,55].

2.2. Copolymerization with polar monomer

Polyethylenes possess essential characteristic like excellent chemical resistance, ease of manufacturing, and low production costs [8]. However, its nonpolar backbone also has a lack of added-value functionalities, which are important applications in many fields [56]. Functionalized polyethylenes exhibit improved surface and mechanical performance due to the incorporation of functional polar groups [19,57]. The synthesis of functionalized polymers is primarily performed by post-polymerization functionalization, free radical copolymerization, or, by use of special methods like ring-opening metathesis polymerization (ROMP). These



Scheme 2. Coordination-insertion mechanism in ethylene copolymerization with polar monomers.

polymerization approaches have some drawbacks, such as the use of harsh conditions or poor controls of polymer microstructure [40,58]. In contrast, flexible synthesis of functionalized polyethylene with well-characterized structures and properties is currently an important field of research in coordination-insertion polymerization [59]. Early-transition metal complexes, like the Ziegler-Natta catalysts, were certainly applied to copolymerize ethylene

with polar monomers. However, researchers could not achieve any success in synthesizing copolymers, due to the poisoning effect from the polar monomers. Thanks to the low oxophilicity, the late-transition metal complexes (especially for Pd-based complexes) exhibit remarkable capacity to copolymerize ethylene with polar monomers (Scheme 2) [11]. Following the insertion of polar monomers, the metal center coordinated with the C=C bond to form the

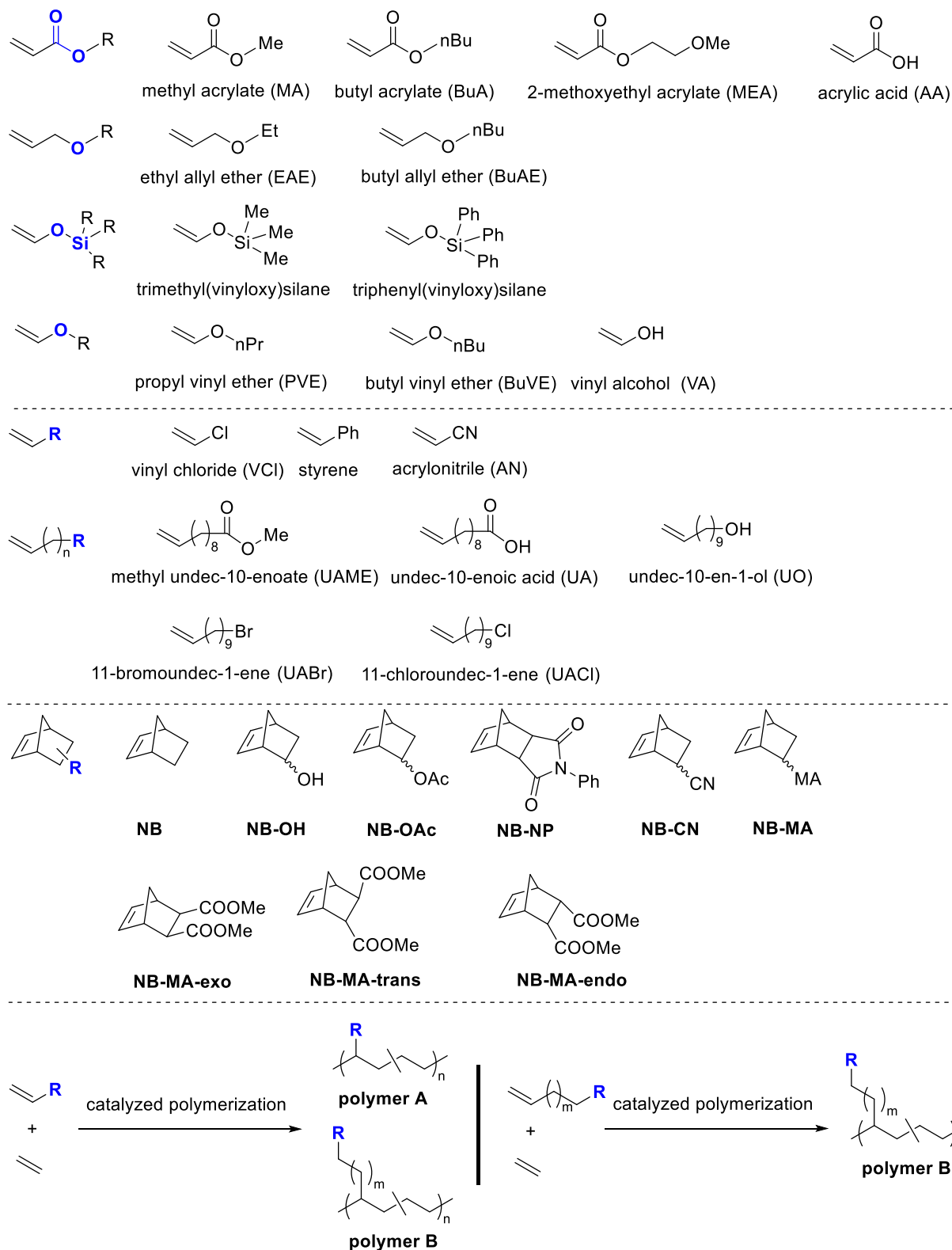


Fig. 2. Representative list of polar vinyl monomers used in ethylene copolymerization.

intermediate I. There were two types of the insertion process, namely the 1,2 insertion (intermediate II) and 2,1 insertion (intermediate III). The polar group, **X** (Lewis-basic groups) and catalytic metal center, **M** (Lewis-acidic groups) in **Scheme 2** potentially generated the stable metalation of X-M chelates. These chelated metalations deactivate the cationic alkyl-metal species and terminate the copolymerization process [5,60].

The initially reported α -diimine Ni and Pd catalysts could surprisingly accomplish the ethylene copolymerization with methyl acrylate as a comonomer [26]. This indicated that the late transition metal catalysts could provide an effective solution for the challenging ethylene copolymerization with polar monomers, because of the low oxophilicity of the metal centers [11,40,61]. This discovery could address the deactivation problems associated with the polar groups near the metal center. However, the field of copolymerization of ethylene and polar monomers has been mainly dominated by the use of α -diimine palladium catalysts. α -Diimine nickel catalysts are generally less tolerant toward polar groups than the palladium catalysts. The nickel catalysts could only catalyze the ethylene copolymerization with a limited number of polar monomers, such as polar derivatives of norbornene, silane-based and long-chain α -olefins [40,62]. With the extensive exploration of new α -diimine Ni and Pd complexes, a variety of polar monomers have been broadly investigated in ethylene copolymerization studies. Fig. 2 displays the collection of polar monomers applied in the ethylene copolymerization catalyzed by α -diimine Ni and Pd complexes. These polar monomers could be classified into two types of vinyl monomers: alkene-connected and long-chain polar monomers [60]. Alkene-connected polar monomers refer to the monomers, where the polar groups were directly connected to the C=C bond. As reported, these types of monomers are the most challenging monomers, potentially poisoning the ethylene copolymerization [47]. Copolymer **A** in Fig. 2 is synthesized from the ethylene copolymerization with alkene-connected polar monomers. These copolymers led to a straightforward attachment of the polar groups to the polymer backbones. The ethylene copolymerization with long-chain polar monomers generates the copolymer **B**, where there is an alkyl spacer between the C=C bond and polar groups. However, copolymer **B** can be generated from the ethylene copolymerization with alkene-connected polar monomers due to the chain-walking process. The functionalized copolymers can even be synthesized with both, in-chain and terminal polar groups, catalyzed by the α -diimine Ni and Pd catalysts. These unique structures of the long-chain polar monomers allowed the easier copolymerization with ethylene, reducing the possibility to poison the catalytic center by means of the coordination with polar sites. This strategy facilitates the polymer products with polar groups away from the polymer backbone. Both types of copolymers (**A** and **B**) provide very interesting and useful properties for future industrial application; and thus, it is currently the driving force in such research field [11,60]. Additionally, polar functionalized norbornenes are also an interesting class of polar substrates (Fig. 2). Ethylene-norbornene (E-NB) copolymers are

an important class of polyolefins with the high refractive index and high transparency. They are suitable for optical applications including lenses, blister packs and medical equipment. As strong π -donors, norbornene-type monomers can efficiently coordinate with the metal centers compared to other polar vinyl monomers. The β -hydride elimination is relatively prevented by the cyclic structure. The presence of long spacers between the C=C bond and the polar groups offers less likeliness for deactivation of the catalytic metal centers [63–66].

3. Recent developments in modified α -diimine Ni and Pd complexes

As mentioned earlier, the α -diimine Ni and Pd complexes are unique in their capacity to control the microstructure of the resulting polymer, while allowing ethylene copolymerization with polar monomers. An additional advantage of the α -diimine Ni and Pd complexes over their early-transition-metal competitors is the ease of synthesis and higher air stability [42,45]. The synthesis largely involves two main reactions (Fig. 3); namely, 1) the α -diimine formation from the reaction of modified anilines and diketones in the presence of the catalytic amount of the acid; 2) the coordination reactions of α -diimine ligands and metal (Ni and Pd) salts or complexes to synthesize α -diimine Ni and Pd complexes. The resulting complexes are very stable to moisture and oxygen. This inertness of α -diimine Ni and Pd catalysts suits the industrial application, where storage stability is a well-known issue. The structural modifications of anilines and diketones initially based on ligands bring about the versatile synthesis of α -diimine Ni and Pd complexes and different coordination environments to the catalytic metal centers.

Generally, the catalytic performance of a metal center is influenced by the electronic and steric effects of the ligand structures [67]. Similarly, previous researchers have reported that high pressures, low polymerization temperatures, bulky backbone substituents, and/or *N*-aryl groups enable polymerization of high-molecular weights, low branching densities, and thus higher melting point [30]. On the other hand, low pressures, high temperatures, and the use of less bulky ligands result in polymers with lower molecular weight, a higher degree of branching, and low melting points. The electronic effects of the ligand are also crucial. Studies on ligands with electron-withdrawing substituents induce the electrophilicity at the catalytic metal center, which indirectly promoted chain propagation, thus enabling higher molecular weight of polyethylene [43,45]. In summary, the catalytic performance can be readily tuned with variations of ligand structures and reaction conditions. In the following section α -diimine complexes are grouped in four classes based on their structural features and reaction conditions, i.e: *N*-aryl modifications (Table 1. and Figs. 4–18), backbone modifications (Table 2. and Figs. 19–23), binuclear complexes (Table 3. and Figs. 24–28), functional group modification (Table 4. and Figs. 29–36).

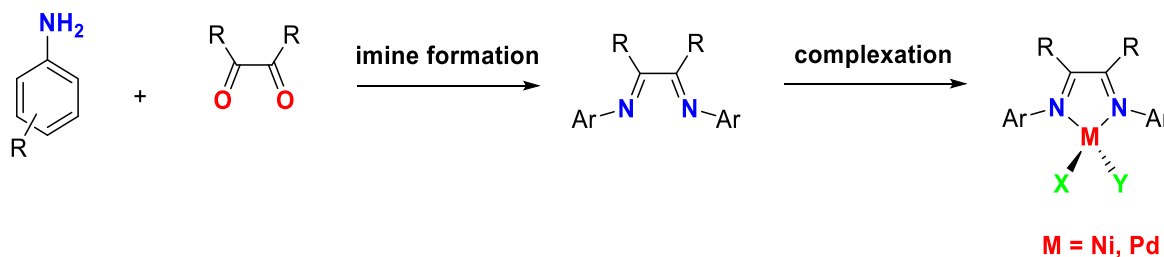


Fig. 3. General approach for the synthesis of α -diimine Ni and Pd complexes.

3.1. N-aryl modification

In recent years, one of the most popular modifications on α -diimine Ni complexes has been the incorporation of the 2, 6-dibenzhydryl group on the *ortho*-N-aryl positions reported by Rhinehart *et al.* in 2013 (Fig. 4)[68]. These α -diimine Ni complexes exhibited remarkable thermal stability in ethylene polymerization. Activated by methylaluminoxane (MAO), the catalytic activity of Ni precatalysts (**C1b** in Fig. 4) as high as 2.81×10^6 g of PE (mol of Ni)⁻¹h⁻¹ at 100 °C (10 min) (Table 1) was estimated. The resulting polymer showed a well-defined and narrow molecular weight distribution ($M_w/M_n \leq 1.31$), moderate degree of branching (63 to 75B/1000C), and high molecular weight ($M_n > 600\,000$ g/mol). The robust nature and thermal stability of **C2** achieved even higher activity (1.4 times in TOFs) than **C1** in ethylene polymerization [69]. An increase in melting point by ~ 20 °C and fewer branching content was also observed for polyethylene. In addition, these Ni complexes exhibited the capacity for living polymerization at 75 °C [70].

Inspired by the **C1** and **C2** structures, Dai *et al.* have further developed the 2, 6-dibenzhydryl-substituted α -diimine Pd complexes (**C3** in Fig. 5) containing either electron-donating (-OMe, -Me) or electron-withdrawing groups (Cl, -CF₃) [71]. In this work, new synthetic strategies led to the improvement in the yield of sterically demanding ligands using the more efficient fashion (yield above 90 %). In comparison to the classical Pd complex **A** (Fig. 1), these Pd complexes exhibited remarkable thermal stability and catalytic properties in ethylene polymerization. Higher catalytic activity up to 3.2×10^6 g of PE (mol of Pd)⁻¹h⁻¹ (60 °C, 15 min) was achieved, accompanied by a higher molecular weight (M_n up to 538 000 g/mol) and lower branching density (23–29B/1000 C) of polyethylenes (Table 1). The melting point (T_m) of the synthesized polyethylene was as high as 99 °C. A semi-crystalline E-MA copolymer was synthesized through Pd-catalyzed copolymerization. It was notable that the slow-chain-walking behaviors of these Pd catalysts resulted in unique polymer microstructures (higher molecular weight and lower branching).

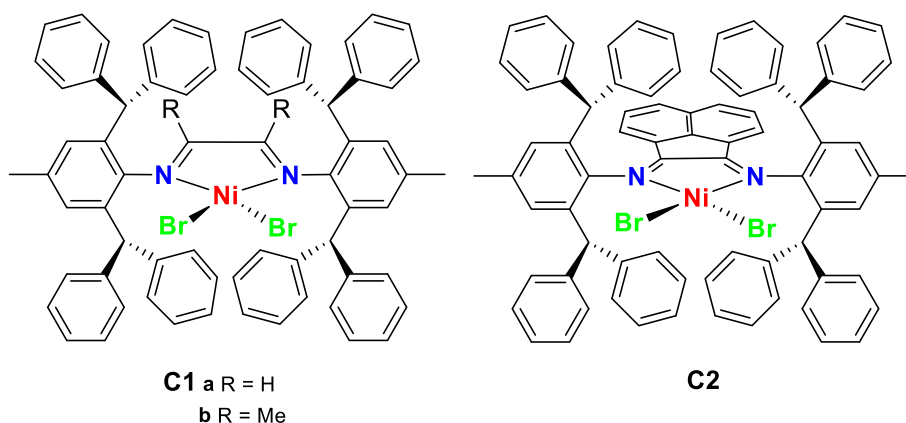


Fig. 4. 2, 6-Dibenzhydryl-substituted N-aryl modification.

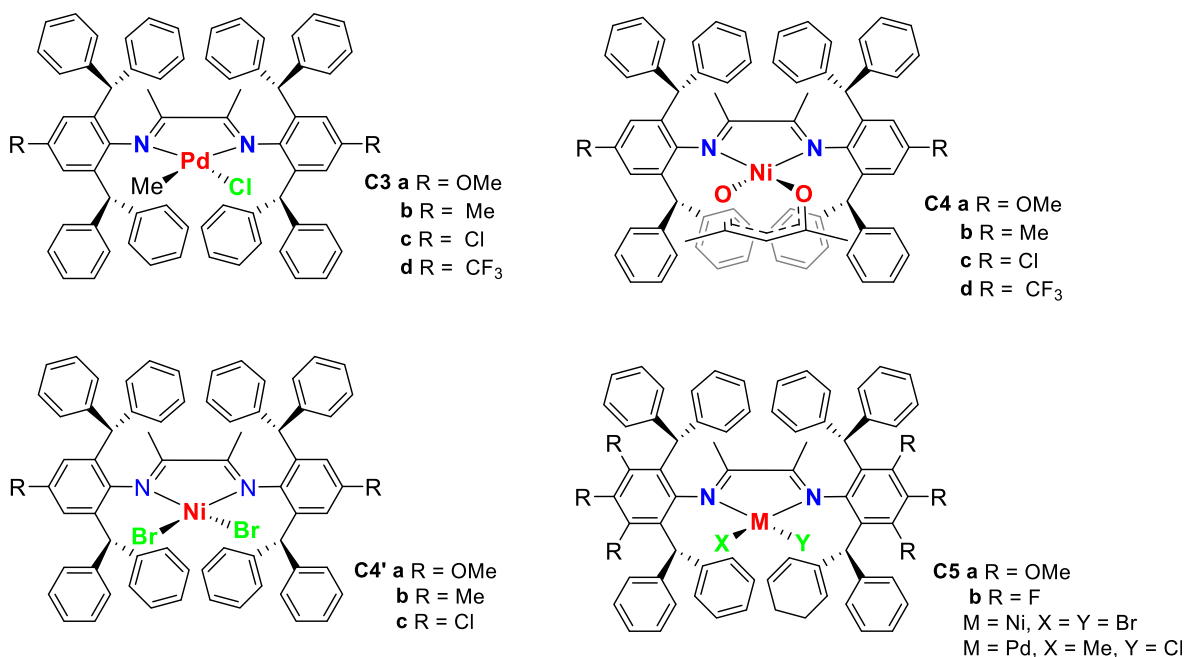


Fig. 5. Functionalized 2, 6-dibenzhydryl-substituted N-aryl modification.

Some new α -diimine Ni complexes (**C4** and **C4'** in Fig. 5) bearing similar coordinating structures as **C3** were synthesized by Guo *et al.* [72]. Namely, **C4** and **C4'** displayed a very high catalytic activity of 6.18×10^6 g of PE (mol of Pd) $^{-1}$ h $^{-1}$ (100 °C, 30 min) (Table 1). The synthesized polyethylene exhibited a molecular weight of more than one million with a rather narrow PDI. All Ni complexes exhibited a robust catalytic behavior combined with high activity, producing a high molecular weight of polyethylenes. Ni complexes were able to polymerize the ethylene even at 100 °C. In the ethylene polymerization, the dibromonickel-catalyzed polymerization was relatively insensitive to the electronic perturbation introduced by structure **C4'**. In contrast, electronic effects of the Ni(acac) systems (**C4**) were clearly observed. Trifluoromethyl-substituted **C4d** catalyst exhibited exceptionally high activity and thermal stability at elevated temperatures.

Simultaneous tuning of both electronic and steric effects was rarely investigated in previous studies. Muhammad *et al.* advanced a series of symmetrical α -diimine Ni and Pd catalysts bearing both benzhydryl *N*-aryl with various substituents of methoxy/fluoro groups (**C5** in Fig. 5) for ethylene polymerization and copolymerization with AA and MA [73]. The six methoxy/fluoro substituents located both at para and meta-positions were able to significantly enhance and alter the electronic effects of ligand and the coordination environment around catalytic metal center. It was hypothesized that the meta-methoxy groups on **C5-Pd-OMe** interacted with the benzhydryl groups, increasing the steric constraints around the metal center. This palladium (**C5-Pd-OMe**) and nickel (**C5-Ni-OMe**) catalysts exhibited an increased catalytic activity [up to 5×10^6 g of PE (mol of Ni) $^{-1}$ h $^{-1}$] (100 °C, 30 min). The resulting polymers had a high molecular weight (2.54×10^6 g/mol) and thus a high melting point ($T_m = 112.2$ °C), along with the reduced polymer branching densities (Table 1). Accordingly, improved mechanical properties were observed. For **C5-Pd-OMe** catalyzed copolymerization, the incorporation of monomer (MA and AA) in the polymer chains were reduced because of the ligand's bulkiness.

In 2018, Guo *et al.* reported a series of sterically hindered and acenaphthene-based α -diimine nickel complexes with the remote R' (-OMe, -Me, -tBu, -Ph) groups in para-positions of diarylmethyl moiety (**C6** in Fig. 6) [74]. Activated by the Et₂AlCl, these nickel catalysts exhibited high activities [up to 5.1×10^6 g of PE (mol of Ni) $^{-1}$ h $^{-1}$] (20 °C, 30 min) and high thermal stability (stable at 100 °C) in ethylene polymerization. The synthesized polyethylenes were characterized as ultra-high molecular weight (UHMWPE) (M_w up to 4.5×10^6 g/mol) with a moderate branching in the range of 26–71B/1000C (Table 1). It was interesting that the presence of remote substituents (-OMe, -Me, -tBu, and -Ph) in the para-

position had a strong influence on the catalytic properties of these corresponding α -diimine nickel complexes and the UHMWPE mechanical properties. These branched UHMWPE materials displayed the typical properties of thermoplastic elastomers with well-defined stress-strain curves and elastic recovery.

More recently in 2020, Xia *et al.* introduced the concerted double-layer steric strategy concept in designing a new series of α -diimine nickel catalysts. This method involved the incorporation of bulky diphenylaniline into the ligand structures (**C7** in Fig. 7) [75]. These newly designed α -diimine Ni and Pd catalysts exhibited both significant thermal stability (stable at 150 °C) as well as very high activity [on the level of 1.03×10^9 g of PE (mol of Ni) $^{-1}$ h $^{-1}$] (30 °C, 1 min) in ethylene polymerization. The resulting polyethylenes exhibited ultrahigh molecular weight ($M_w = 4.2 \times 10^6$ g/mol) with a controlled degree of branching from quasi-linear (2B/1000C) to lightly branched (32B/1000C) structures (Table 1). Ethylene copolymerization with a good incorporation of methyl 10-undecenoate was also observed. The key structural innovations introduced in **C7** explained its typical catalytic performance. The first steric layer offered by the inner phenyl rings provided enough space for ethylene coordination and insertion. The second steric layer from outer phenyl rings gave rise to restraining chain transfer. This strategy of catalyst design led to simultaneously high catalytic activity and high molecular weight of polyethylene, normally better than the reported conventional modifications.

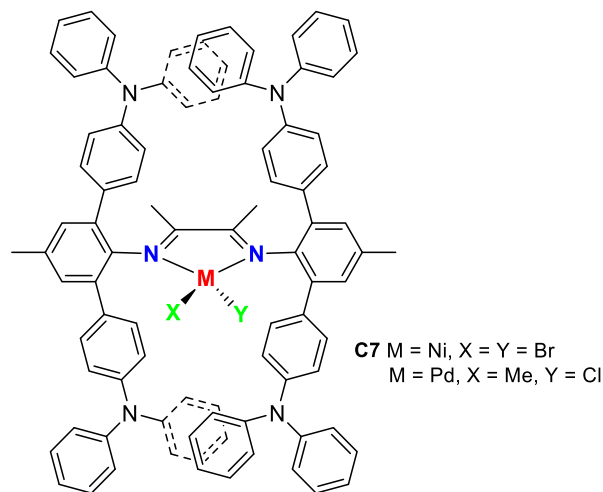


Fig. 7. Concerted double-layer steric strategy for *N*-aryl modification.

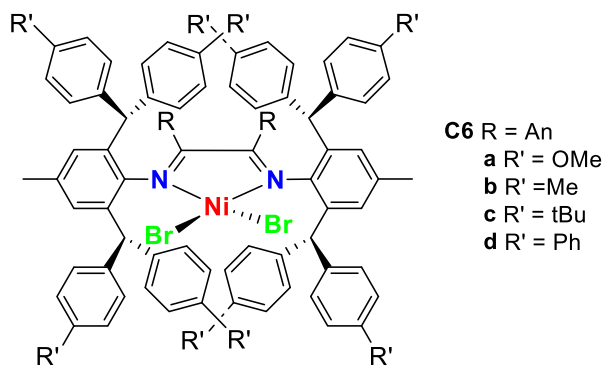
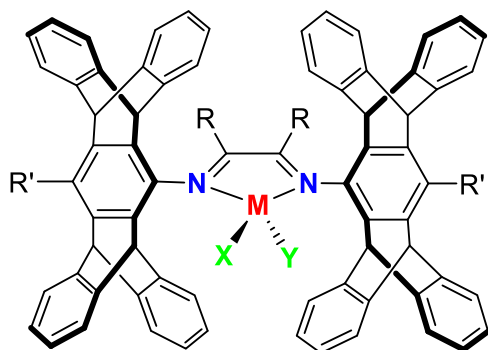


Fig. 6. para-Position functionalized 2,6-Dibenzhydryl-substituted *N*-aryl modification.

Kanai *et al.* initially reported the Ni complexes with symmetric bowl-shaped α -diimine ligands, consisting of two pentiptyceny-substituents in [(α -diimine)NiBr₂] (**C8a** in Fig. 8). The Ni complexes displayed good catalytic activity in ethylene (co)polymerization [76]. The Et₂AlCl/**C8a** system exhibited a moderate catalytic activity of 3.4×10^4 g of PE (mol of Ni) $^{-1}$ h $^{-1}$ (25 °C, 30 min) at 7 atm. The molecular weight of the resulting polyethylene reached up to 1.5×10^5 g/mol with low branching densities (12B/1000C) and a high melting point of 133 °C. The catalytic performance of these complexes structures was attributed to the coordination environment of nickel, which was located in a highly shielded, hemispherical, and crowded space of the two pentiptycene units. Polar monomers (UAME, UA, UCl, and UO in Fig. 2) and ethylene could be efficiently copolymerized, leading to the copolymers with 4.2 mol% incorporations of polar monomers. The copolymerization highly depended on the amount of activator and was relative to the amount of polar monomer. By lowering the molar ratio of Et₂AlCl/

**C8****Fig. 8.** Bulky pentiptycenyly substituted *N*-aryl modification.

- a** R, R' = OBU, Me
b R, R' = OH, An
c R, R' = OMe, An
d R, R' = OMe, Me
f R, R' = OBU, An

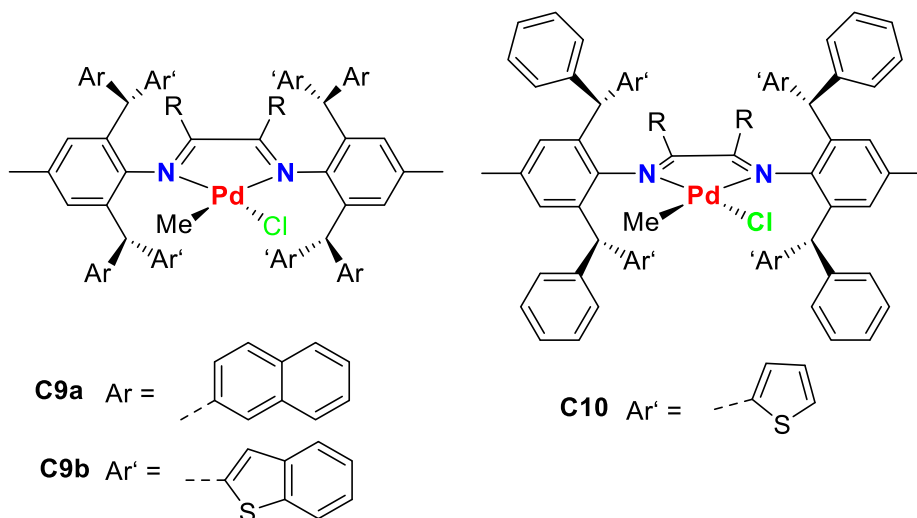
M = Ni, X = Y = Br
 M = Pd, X = Me, Y = Cl

polar monomer to 0.5, the decreased activity for ethylene copolymerization with oxygen-containing monomers was observed, while 11-chloro-1-undecene could still be efficiently copolymerized with ethylene under the same conditions.

Similar to the above work, *Liao et al.* then proposed a novel series of sterically demanding pentiptycenyly *N*-aryl substituted α -diimine Ni and Pd catalysts for ethylene (co)polymerization (**C8b** to **f**) [77]. These newly synthesized complexes were characterized as highly bulky substituents and backbone. For ethylene polymerization (20–80 °C) catalyzed by Ni complexes, the catalytic activities were in the range of 0.64 to 3.74×10^6 g of PE (mol of Ni)^{−1}h^{−1} (60 °C, 30 min). The generated polyethylenes exhibited a moderate molecular weight of 3.77×10^5 g/mol, tunable branching densities from 6B/1000C to 55B/1000C, and high T_m (135 °C) (Table 1). These Pd catalysts ensured respectable MA incorporation up to 4.1 mol% in the copolymerization with ethylene. Compared with the free rotation of dibenzhydryl substituents, the restricted rotation of pentiptycenyly substituents offered superior activity and a slower chain-walking process for α -diimine Ni(II) species. These special bulky groups also enhanced comonomer incorporation for α -diimine Pd(II) species. It was notable that less steric blockage of substituents at the axial posi-

tions on the catalytic metal center led to a decrease in the molecular weight of the resulting polymer.

In 2016, *Dai et al.* reported the synthesis of novel naphthalene and benzothiophene substituted *N*-aryl groups on α -diimine Pd complexes (**C9a**, **C9b** in Fig. 9) [78]. In ethylene polymerization, these Pd complexes displayed the moderate catalytic activity around 4.1×10^5 g of PE (mol of Pd)^{−1}h^{−1} (60 °C, 15 min) and good thermal stability (Table 1). The produced polyethylenes achieved extremely high molecular weights (8.02×10^6 g/mol), low branching densities (as low as 6B/1000C), and comparatively high melting points (T_m up to 127.2 °C). In ethylene-MA copolymerization, the catalytic activity was in the order of 3.03×10^4 g of PE (mol of Pd)^{−1}h^{−1}. The E-MA copolymer possessed rather high molecular weights (*M_n* up to 4.42×10^5 g/mol). The initial α -diimine catalyst **A** (Fig. 1) was deactivated in the presence of a long-chain polar monomer, which was speculated to the fast chain-walking process of catalyst **A**. Compared to catalyst **A**, **C9a** and **C9b** were more efficient in the copolymerization of long-chain monomers achieving high activity. The molecular weight of the copolymers was close to 1×10^6 g/mol. The surface wetting property of the resulting polymer was indeed improved via this incorporation of the polar functional groups into the polymer chains.

**Fig. 9.** 2,6-Diaryldiaryl-substituted *N*-aryl modification.

In 2018, Na *et al.* demonstrated the specially designed α -diimine Pd complex containing steric thienyl-phenyl substitution (**C10** in Fig. 9) [79]. The properties of hence generated polyethylene were similar to low-density polyethylene (LDPE). Tunable branching densities (16 to 37B/1000C), high melting points (T_m 101 to 113 °C), and low polymer densities (0.89–0.92 g/cm³) were observed. Polar-functionalized low-density polyethylene (P-LDPE) was synthesized via ethylene copolymerization with polar monomers. The catalytic activities during copolymerization were up to 10⁵ g of PE (mol of Pd)⁻¹h⁻¹. Copolymers with high incorporation (6.8 %), high molecular weights (M_n up to 1.24×10^6 g/mol), high melting points (118 °C), and tunable branching densities (14 to 46B/1000C) were achieved. The incorporation of polar groups significantly influenced the mechanical as well as the surface wetting properties of the resulting copolymers.

Rishina *et al.* investigated the catalytic effects from fluoro (**C11a**) and trifluoromethyl (**C11b**) substituted *N*-aryl modifications on α -diimine Ni catalyzed ethylene and propylene oligomerization (Fig. 10) [80]. Oligomerization of ethylene with **C11** activated by a mixture of Et₂AlCl /EASC and PPh₃ at 30 °C resulted in only oligomers (i.e. oligomerization degree: 6 to 9) as mixtures of wax and liquid. A microstructure study indicated that the oligomers contained 14 to 20 mol% of methyl branches, 4 to 6 mol% of ethyl branches, and a small number of long-chain branches. In propylene oligomerization, these catalysts produced mixtures of very short oligomers (mostly dimers) at elevated temperatures from 30 to 70 °C. **C11bNi** generated the active species that exhibited no regioselectivity. Compared with **C11b**, the preference for primary insertion was observed in the oligomerization catalyzed by the **C11a Ni** complex.

Mundil *et al.* designed the series of α -diimine Ni and Pd complexes bearing fluorinated alkyl substituents at the *para*-*N*-aryl groups **C12** (Fig. 10) [81]. These complexes were used to carry out catalyzed polymerization of ethylene, propene, and 1-hexene. Remarkably, there were no significant effects on the catalytic properties due to fluoroalkyl groups. The branching densities of the generated polyolefins were rather tunable by the ligand's backbones and *ortho*-substituents of *N*-aryl groups.

In 2017, Lian and Wang *et al.* reported the novel synthesis of PTPE-type polyethylenes through ethylene polymerization, which was catalyzed by the Xanthene substituted *N*-aryl of α -diimine Ni and Pd (**C13** in Fig. 11) [82,83]. These α -diimine Ni complexes revealed rather high activities [up to 6.94×10^6 g of PE (mol of Pd)⁻¹h⁻¹] (20 °C, 30 min) and thermal stability at 80 °C for ethylene polymerization. The generated polyethylenes exhibited high molecular weight (M_n up to 1.53×10^6 g/mol) and notably narrow molecular weight distributions (Table 1). The remote substituents (-Ph, -CF₃, -NO₂, and -OMe) had again a dramatic influence on the catalytic properties of ethylene polymerization. Specifically, the nickel complexes bearing the -Ph substituent (**C13Ni-Ph**) led to the formation of polyethylenes with exceptional elastic properties due to the branched structure of polyethylene (elastic strain recovery value of 70 % via **C13Ni-Ph** at 40 °C). The catalytic properties of Pd complexes were investigated in ethylene polymerization and ethylene/MA, ethylene/NB, ethylene/5-norbornene-2-yl acetate copolymerization. High molecular-weight E-MA and E-NB copolymers were produced by Pd-catalyzed copolymerization. **C13Pd-Ph** exhibited much higher activity (up to 2.5×10^4 g of PE (mol of Pd)⁻¹h⁻¹) than other complexes, and generated polymers and copolymers with much higher molecular weight (M_n up to 1.21×10^5 g/mol).

In 2017, Li *et al.* investigated a series of α -diimine Ni and Pd complexes bearing nitrogen-containing cyclic groups (**C14** in Fig. 12) [84]. In ethylene polymerization, the nitrogen atoms situated on *N*-aryl groups of **C14a** and **C14b** interacted with catalytic metal centers in a remarkable manner. The catalytic metal center was then highly tolerant to polar functional groups, while the polymer branching densities were significantly reduced. The generated polyethylenes were characterized as nearly perfect linear structure (branching < 1B/1000C and high T_m (>130 °C) (Table 1). For the unsymmetrical Pd**C14c**, a moderately branched polymer (around 70B/1000C) was produced. The presence of nitrogen also improved the thermal stability of the catalysts. Continuously high activity was achieved in polymerization even after 2 h at 60 °C, while the high molecular weight of polymers was still achieved at 80 °C. Additionally, these newly designed α -diimine Ni and Pd complexes

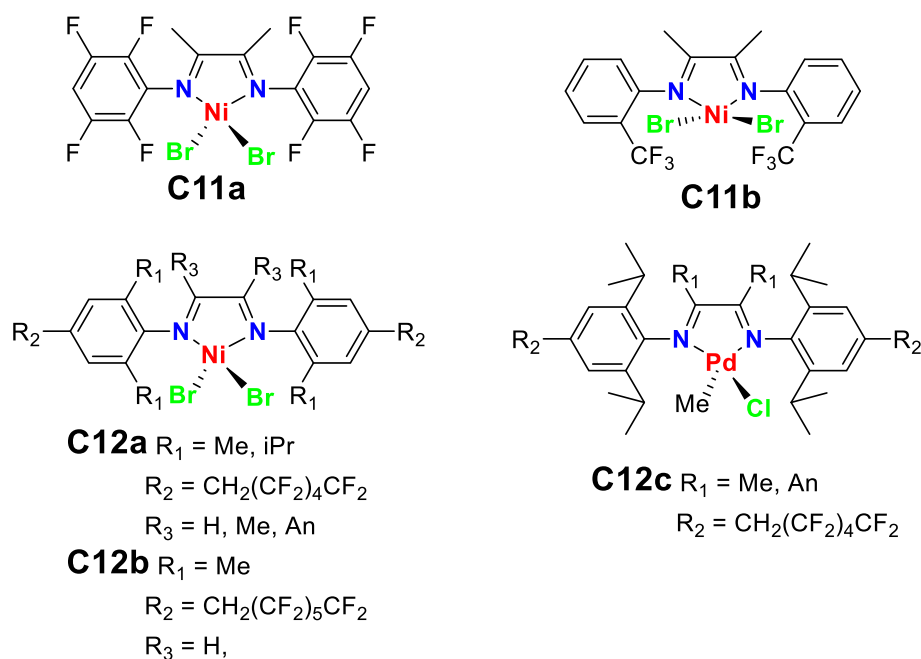
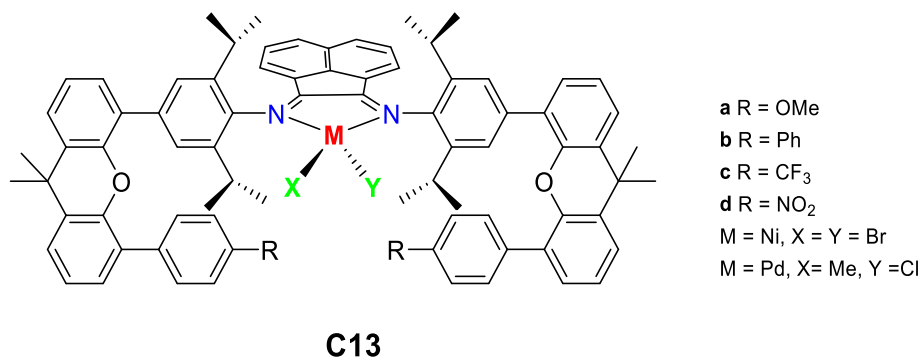
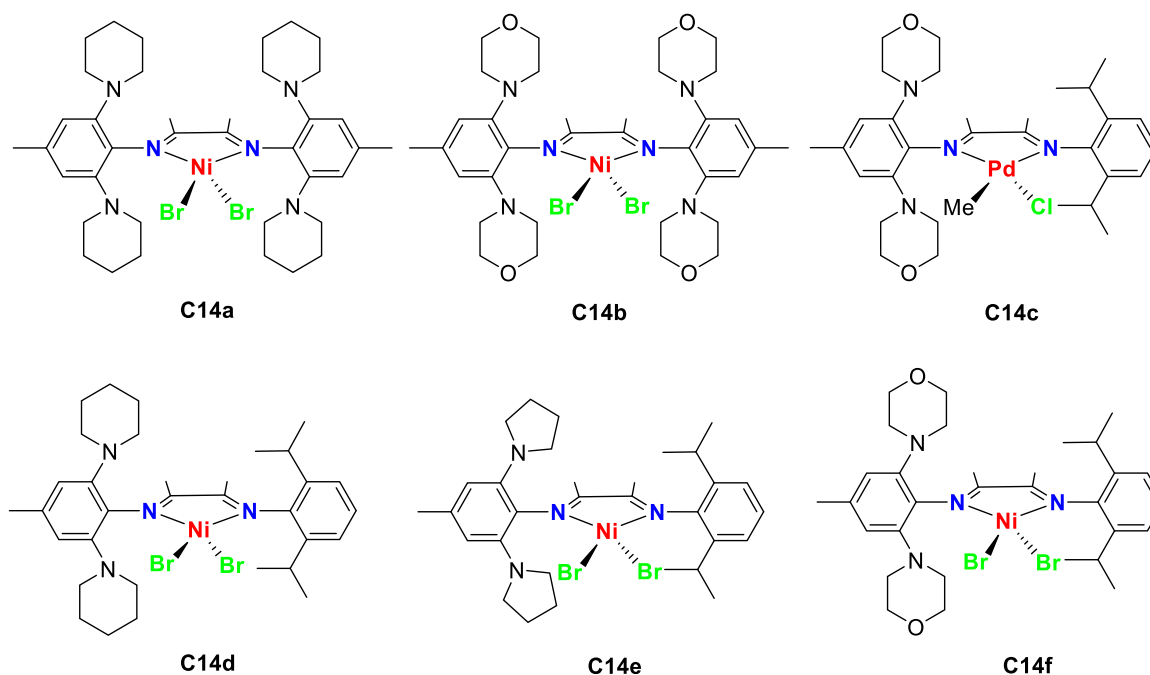


Fig. 10. Fluoro- and trifluoromethyl substituted *N*-aryl modification.

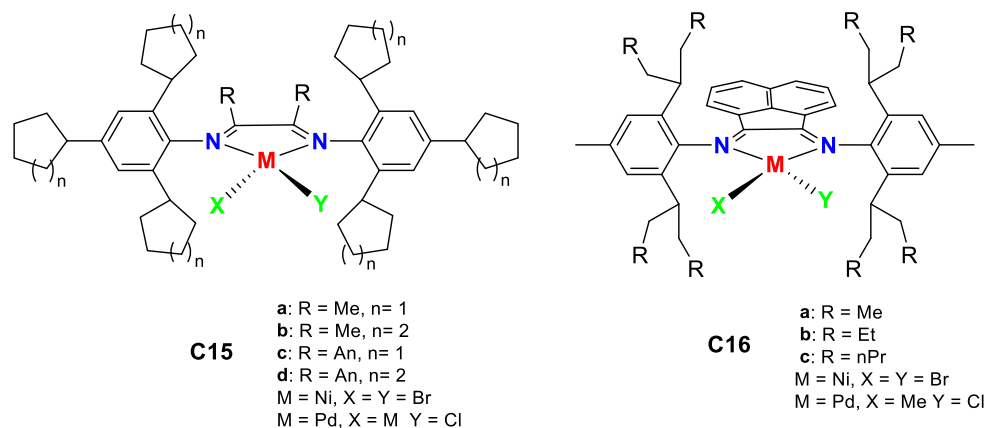
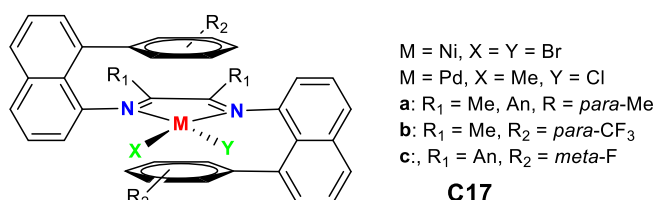
Fig. 11. Xanthene substituted *N*-aryl modification.Fig. 12. Nitrogen-containing ring-substituted *N*-aryl modification.

were able to copolymerize ethylene with a series of polar comonomers such as UAME and the challenging AAc. Linear E-MA copolymers with high incorporation (up to 7.5 mol%) were still achieved in copolymerization. Furthermore, the functional-group tolerance of the catalytic metal center was greatly enhanced by the presence of additional side-arm heteroatoms. The high tolerance and unique catalytic performance were attributed to a “second-coordination sphere” strategy. It was hypothesized by the author that a second coordination sphere of the ligands was stronger than β -H or β -X (X being a polar group). Nevertheless, the activity was still weaker than with ethylene insertion. It was noteworthy that the experimental data and the hypothesis was backed up by a computational study.

Compared to rigid steric modifications, Guo and Dai *et al.* worked with a series of flexible alkyl (**C15**) and cycloalkyl (**C16**) substituted *N*-aryl units of α -diimine Ni and Pd complexes (Fig. 13) [85,86]. Compared with fixed phenyl substitutions on α -diimine Ni complexes (**B** in Fig. 1), the flexible cyclohexyl complexes exhibited distinctive catalytic behavior. The polymers were generated with remarkably high branching densities, low T_m , and low molecular weight. PTPE-type polymers with these highly branched polyethylenes were obtained. The flexible cyclohexyl

Pd catalyst exhibited a remarkably higher catalytic activity than the conventional α -diimine complexes (**A** in Fig. 1), providing an increased amount of molecular weight and branching density in ethylene (co)polymerization. The flexible modification of cyclohexyl α -diimine Ni and Pd complexes offered a much faster chain-walking process and higher catalytic activity. The synthesized polymers possessed higher molecular weight with appreciable comonomer incorporation. In terms of long-chain alkyl α -diimine Ni and Pd complexes, the Ni complexes presented high activities [up to 2.14×10^6 g of PE (mol of Ni)⁻¹h⁻¹](20 °C, 30 min) and generated highly branched polyethylene with ultra-high molecular weight (M_n up to 1.2×10^6 g/mol) (Table 1). The synthesized polyethylene also displayed exceptional capacity in mechanical elasticity like TPE-type polymers (SR value up to 88 %).

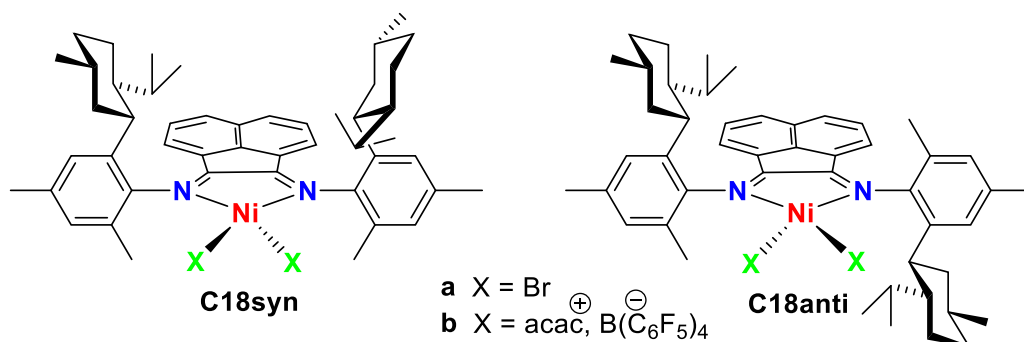
Brookhart *et al.* have described two “sandwich-like” arrangements of naphthyl substituted *N*-aryl groups in α -diimine Ni-based precatalysts (**C17aNi** in Fig. 14) [87]. The two 8-p-tolynaphthylimino moieties were implanted on the α -diimine ligands to shield the Ni-axial direction and thus control the monomer insertion. The tolyl substituents are arranged perpendicular to the naphthyl rings, which were nearly coplanar with the square coordination plane. Activated by the modified methylalumoxane,

Fig. 13. Cycloalkyl and alkyl-substituted *N*-aryl modification.Fig. 14. “Sandwich”-type naphthyl substituted *N*-aryl modification.

these distinctive Ni complexes produced hyper-branched (up to 152B/1000C) polyethylenes with high molecular weights. It was believed that the increased axial bulk efficiently led to lower rates of chain transfer, relative to increase the chain propagation rates. Meanwhile, it resulted in high molecular weights and narrow PDIs of polyethylene. Subsequently, Vaidya *et al.* have developed additional similar derivatives of “Sandwich”-type nickel complexes (**C17bNi**) [88]. They were applied to catalyze higher α -olefin polymerizations with precise control of the chain-walking process, which favors the ω , 1-enchainment. The “sandwich” type catalysts also provided the chance to synthesize the low-branched polyethylene with a “chain-straightened” semi-crystalline property (high melting point). With the activation of MAO, O'Connor *et al.* then used the **C17bNi** complex to generate polyolefin-based PTPE-type block copolymers (Table 1). The 1-decene monomer was responsible for high crystallinity and hard blocks, while low crystallinity soft blocks were synthesized from ethylene monomer [89]. Various

block structures were characterized as copolymers in the range of block size from diblock to heptablock. All resulting polymers behaved as elastic PTPE-type materials. More recently, Allen *et al.* have reported newly synthesized “sandwich” types of α -diimine palladium catalysts (**C17aPd** in Fig. 14) for ethylene polymerization [90]. The Pd complexes were used in the ethylene polymerization with typical signs for living polymerization at 25 °C. The resulting polyethylene was hyper-branched and exhibited narrow molecular weight distribution (around 1.1). Ethylene copolymerization with MA using the Pd catalysts presented a high percentage of incorporation, which was up to 14 %.

Zhai *et al.* reported a new *ortho*-menthyl substituted *N*-aryl on the α -diimine Ni complexes as the *syn*- and *anti*-conformers for ethylene and 1-hexene polymerization (**C18** in Fig. 15) [91]. Both *anti*- and *syn*-conformers of **C18b** could be activated by the Et₂AlCl for polymerization. The catalytic activity could be achieved from 2.5 to 6.6 $\times 10^6$ g of PE (mol of Ni)⁻¹h⁻¹ (15 psi of ethylene pressure at room temperature and 15 min) in ethylene polymerization (Table 1). The *syn*- and *anti*-conformers of **C18** exhibited a different catalytic performance. The polyethylene produced by *syn*-conformers tends to entail a higher molecular weight and branching density than the one obtained from the *anti*-conformer catalyzed polymerization. Compared to polyhexene produced from *anti*-conformer, the polymer produced by *syn*-conformer possessed a higher level of chain straightening and a higher percentage of methyl branches rather than butyl branches. This result also indicated a greater preference for the 2,1-insertion and chain-walking process for the *syn*-conformer **C18syn**.

Fig. 15. *ortho*-Menthyl substituted *N*-aryl modification.

In recent years, Sun *et al.* contributed considerable research towards the α -diimine Ni-catalyzed ethylene polymerization [45]. All finely tuned α -diimine nickel complexes in Fig. 16 are selected examples of such modifications on the *N*-aryl groups [92–112]. The Ni complexes exhibited outstanding catalytic activity and generated polyethylene of high molecular weight and highly branched microstructures. For instance, **C19Ni** were unsymmetrically synthesized with various and modified benzhydryl substitutions on one of the two *N*-aryl groups. Activated by MAO, MMAO, Et_2AlCl , or EASC, a remarkable catalytic activity of 1.48×10^7 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$ could be reached. Super highly branched polyethylene with branching densities as high as 337B/1000C were obtained. The polymer produced solely by ethylene monomer exhibited typical PTPE properties. The molecular weight of the resulting polyethylene was in the range of 10^5 to 3×10^6 g/mol, which is characteristic of UHMWPE and it exhibited a narrow molecular weight distribution (Table 1). Complexes **C20** were synthesized with the incorporation of a 2,4- or 2,4,6-substitution pattern using the steric benzhydryl groups. As a remarkable feature, high activity was retained at the high thermal stability of these catalysts. Activated by MMAO cocatalyst, **C20aNi** (*ortho*-R group as -Me) exhibited high activities of up to 8.9×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$ and resulted in highly branched polyethylenes (166B/1000C) at 80 °C. In presence of relatively low amounts of EASC, **C20bNi** exhibited higher activities compared to **C20aNi** [up

to 10.9×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$], retained thermal stability by maintaining high activity (3.76×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$) at 80 °C. **C20c** with the 2,4,6-substituted benzhydryl presented remarkable activity even at 90 °C [2.97×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$]. The synthesized polyethylene contained hyper-branched microstructures as high as 135B/1000C, which were analyzed as methyl (84.4 %), ethyl (5.6 %), and longer chain branches (10 %). **C21** containing *N*-naphthyl ligands displayed moderate activity. Activated by either MAO or Et_2AlCl , **C21** yielded polyethylene with typically low branching densities and a high melting point (131 °C). The catalytic performance of unsymmetrical *N*-naphthyl complexes **C22** was investigated to determine the influence of the bulky difluorobenzhydryl substitution. With the activation of Et_2AlCl , **C22** exhibited high activity, exhibiting a narrow molecular weight of polyethylene (1.22–1.99). Activated by MAO and Et_2AlCl , **C23aNi** showed high activities in ethylene polymerization with the activity of up to 10^7 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$, illustrating the feature of the single-site active species and observing narrow molecular weight distributions of the resultant polyethylene. **C23bNi** exhibited higher activity over **C23aNi**, which was ascribed to the electron withdrawing nature of the *para*-fluorides and their influences on the active metal centers. **C23cNi**/EASC system generated both high activity and thermal stability, catalyzing the ethylene polymerization effectively even at 80 °C [6.01×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$ (30 min)], while yielding high

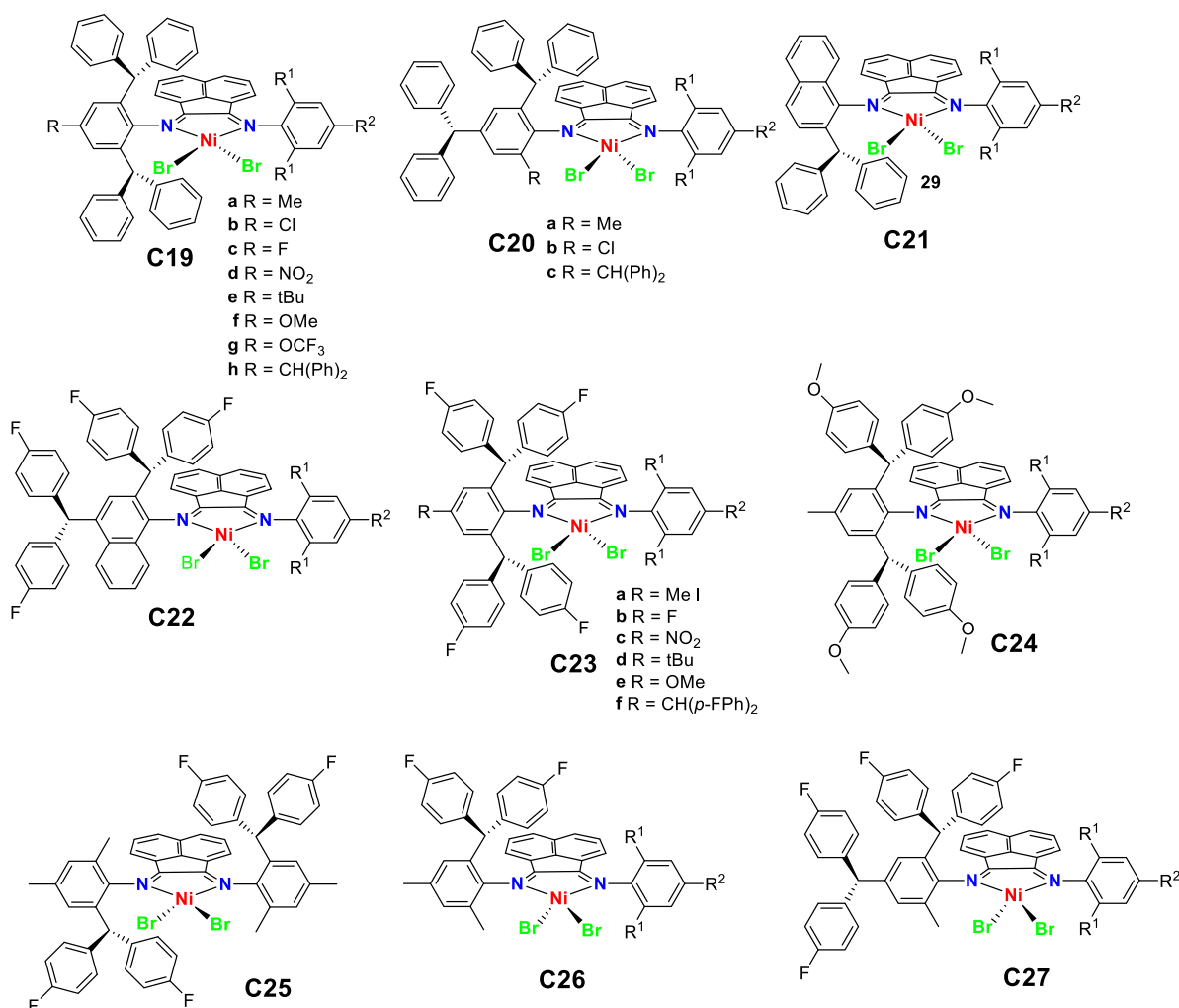


Fig. 16. Unsymmetrically steric and electronic enhancement substituted *N*-aryl modification.

molecular weight (as high as $10.6 \times 10^5 \text{ g mol}^{-1}$) polymers for the same reaction time. Notably, the polyethylene produced by **C24Ni** was characterized as ultra-high molecular weight ($>1 \times 10^6 \text{ g mol}^{-1}$) with a relatively high degree of branching (115 branches per 1000 carbons). **C25Ni** and **C26Ni** displayed a moderate catalytic activities up to $10^6 \text{ g of PE (mol of Ni)}^{-1}\text{h}^{-1}$ (30 min) upon the activation with either MAO and EASC. Particularly, **C26Ni** exhibited good thermal stability in the temperatures range from 60 to 80 °C, generating the polyethylenes with high molecular weight. Activated by either MAO or Et_2AlCl , **C27Ni** exhibited outstanding catalytic activity in ethylene polymerization [$1.02 \times 10^7 \text{ g of PE (mol of Ni)}^{-1}\text{h}^{-1}$ (30 min)]. **C27Ni** bearing the equivalent difluorobenzhydryl-substituted *N*-aryl groups was observed to have exceptional thermal stability. **C27Ni**/ Et_2AlCl system exhibited high activity [$1.02 \times 10^7 \text{ g of PE (mol of Ni)}^{-1}\text{h}^{-1}$ (30 min)] at 100 °C, while generating the polyethylene with the high molecular weight. Significantly, the polyethylenes possessed exceptional elastomeric recovery and high elongation at break determined by DMA and stress-strain testing. In summary, these research offered a promising route to alternative materials for the conventional thermoplastic elastomers (TPEs).

Zhai et al. reported a series of novel α -diimine Pd complexes containing the secondary amide ($-\text{CONHMe}$) or tertiary amide ($-\text{CONMe}_2$) substituents on the *N*-aryl groups (**C28** in Figure 17) [113]. These Pd complexes were investigated in the catalytic performance of ethylene polymerization, ethylene/MA, and ethylene/AA copolymerization. With the replacement of two *i*Pr units using $-\text{CHPh}_2$ groups, **C28** led to a significant improvement in catalytic performance. The generated (α -diimine) PdMe^+ species (**C28**) were activated by NaBAR_4^F to produce polyethylenes with a molecular weight of around $5.9 \times 10^4 \text{ g/mol}$. Compared to **C29**, the structure **C28** exhibited lower catalytic activity [$3.9 \times 10^4 \text{ g of PE (mol of Pd)}^{-1}\text{h}^{-1}$] (20 °C, 120 min) (Table 1). This was due to the enhanced steric effects of $-\text{CHPh}_2$ groups, which counteracted the negative effect of electron-withdrawing amide units. The resulting polymers exhibited moderate branching content (77 to 81B/1000C). In addition, the Pd complex of **C28** incorporates higher levels of MA and AA in the copolymerization with ethylene than **C29**.

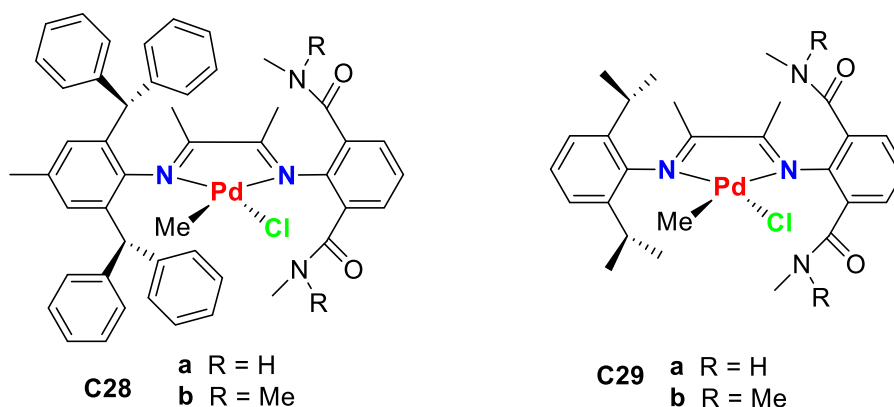


Fig. 17. Unsymmetrical amide substituted *N*-aryl modification.

Hu et al. recently reported the newly developed α -diimine Ni and Pd complexes with the steric enhancement of unsymmetrically pentiptycenyldibenzhydryl substituted *N*-aryl modifications (**C30** in Fig. 18) [114,115]. It demonstrated some new catalytic features of **C30** compared to previous studies [45]. Within a relatively long-lived reaction time, the increased bulk of α -diimine Ni and Pd complexes indeed raised the molecular weight of polyethylene, while this trend differed in the short polymerization time. With increased steric, the branching density initially increases followed by a decrease. In Ni-catalyzed ethylene polymerization, the activity can be as high as $6 \times 10^6 \text{ g of PE (mol of Ni)}^{-1}\text{h}^{-1}$ (20 °C, 5 min), producing the polyethylene with ultrahigh molecular weight ($1.58 \times 10^6 \text{ g/mol}$) (Table 1). The **C30Ni** enabled the ethylene copolymerization with UAME, generating copolymers with high molecular weight ($2.13 \times 10^5 \text{ g/mol}$) and branching density (138B/1000C). Compared to **C30Ni**, the catalytic activity of **C30Pd** is comparatively lower.

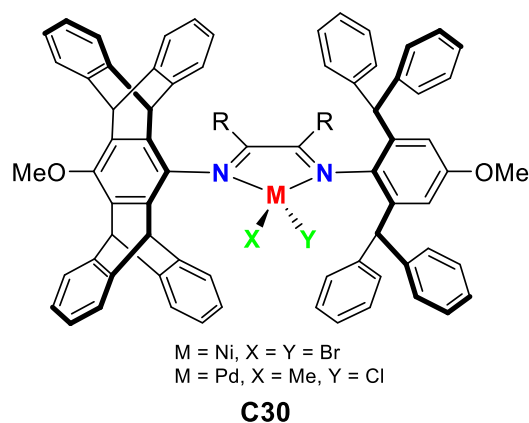


Fig. 18. Unsymmetrical pentiptycenyldibenzhydryl substituted *N*-aryl modification.

Table 1Representative ethylene polymerization catalyzed by *N*-aryl modified α -diimine Ni and Pd catalysts.

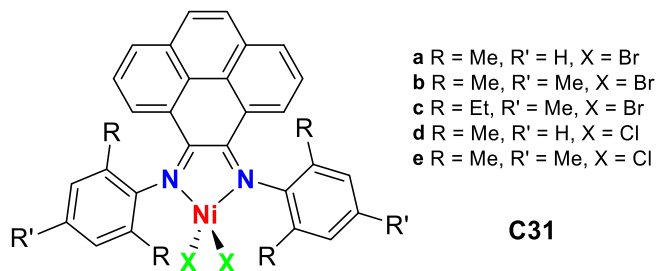
C-Ni/Pd ^a	Co-cat.	T (°C)	t, min	Cat. ^b	P ^c	M _w ^d	PDI ^d	T _m (°C) ^e	B/1000C ^f	Ref.
C1b	PMAO-IP	100	10	2.81	7	0.53	1.24	46	–	[68]
C2	PMAO-IP	100	5	13.5 ^{b'}	7	0.37	1.45	59	52	[69]
C3	NaBARf	60	15	3.2	9	0.15	1.77	94	26	[71]
C4b	MAO	60	30	2.62	9	2.16	1.40	39.1	66	[72]
C4'd	Et ₂ AlCl	100	30	6.18	9	1.23	2.14	41.5	62	[72]
C5a	MAO	100	30	5	9	4.10	1.6	79.3	38	[73]
C6d	Et ₂ AlCl	20	30	5.10	7	2.96	2.24	107.3	26	[74]
C7b	MMAO	30	1	1026	8	4.20	1.58	130	2	[75]
C8d	MAO	60	30	3.74	6	1.20	4.6	118	38	[77]
C9b	NaBARf	60	15	4.10	8	0.52	1.23	119.0	20	[78]
C12c	MAO	25	30	10.80 ^{b'}	2	0.28	2.09	83.0	49	[81]
C13a	MAO	20	30	6.94	9	0.24	2.21	50.1	61	[82]
C14f	MAO	RT	60	0.13	8	1.02	1.72	59	58	[84]
C15b	MAO	20	30	2.14	6	0.11	1.91	38	84	[85]
C16b	MAO	50	30	4.80	6	0.29	1.97	–16	92	[86]
C17	MMAO	50	30	104 ^{b'}	13.6	0.23	3.6	59	94	[87]
C18anti	Et ₂ AlCl	22	15	6.6	4.8	0.25	2.4	113.4	19	[91]
C19e	Et ₂ AlCl	30	30	5.88	10	3.08	2.4	53.4	–	[96]
C28	NaBARf	25	120	0.04	13	0.69	1.53	–	77	[113]
C30	Et ₂ AlCl	30	5	6.00	8	1.58	2.29	76.0	67.3	[114]

^a α -diimine Ni and Pd complexes.^b activity: $\times 10^6$ g of PE (mol of M)^{–1}h^{–1}.^{b'} activity: Turnover frequency (TOF) = mol ethylene/(mol cat h), $\times 10^4$ h^{–1}.^c ethylene pressure in bar/atm.^d determined by GPC, $\times 10^6$ g/mol, PDI as polydispersity index.^e determined by DSC.^f branching density: Branches per 1000 carbon.

3.2. Backbone modification

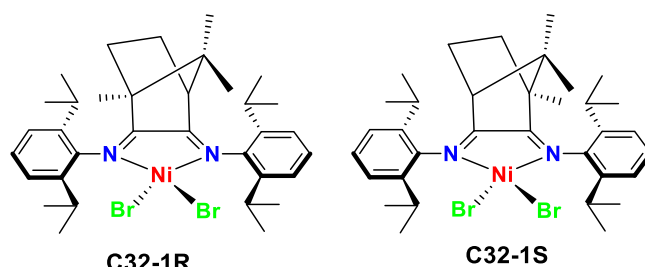
A substantial class of structural variations relates to modifications at the reactive center backbone in the catalyst. The table below summarizes structures **C31–C38** and each of these structural variations will then be described in detail below.

Song *et al.* explored the synthesis and characterization of α -diimine Ni dihalides (Cl and Br), bearing the 4,5-bis (arylimino) pyrenylidene (**C31** in Fig. 19) [116]. After activation with a very low amount of cocatalysts including MAO, EASC, and Et₂AlCl, the structure **C31** exhibited high activity up to 4.41×10^6 g of PE (mol of Ni)^{–1}h^{–1} (40 °C, 30 min) (Table 2). The microstructure of the synthesized polyethylene was analyzed using high temperature NMR, which revealed a high degree of branching density (up to 130B/1000) and narrow molecular weight distributions (around 2.5). This work also indicated that reaction parameters like the Al/Ni molar ratios, the reaction temperature, and polymerization time had a significant influence on the catalytic activity and the properties of the generated polyethylenes.

**Fig. 19.** 4,5-bis (arylimino)pyrenylidene substituted backbone modification.

Liu *et al.* proposed two chiral α -diimine Ni complexes containing (1R)- and (1S)- camphyl substituted backbone for ethylene and α -olefin polymerization (**C32** in Fig. 20) [117]. In this catalytic system, the chiral tunes on the ligand structure exhibited no influ-

ences on the catalytic behavior and region-selectivity for the Ni catalyzed polymerization. Activated by Et₂AlCl, the catalytic activity of **C32** revealed characteristics of a living polymerization for ethylene, propylene, 1-hexene, and 4-methyl-1-pentene under the optimized conditions (Table 2). Rather narrow molecular weight distributions (PDI < 1.2) were observed in the produced polypropylenes and poly(1-hexene)s with a wide range of polymerization temperatures. A high 1,3-enchainment fraction of 45 % was also observed in **C32Ni**-catalyzed propylene with polymerization at –60 °C, which was attributed to the 2,1-insertion of propylene and a chain-walking process.

**Fig. 20.** Chiral camphyl substituted backbone modification.

Zou *et al.* reported a series of α -diimine Ni(II) and Pd(II) complexes with different substituents on the acenaphthyl backbones (**C33a–e** in Fig. 21) [118]. The corresponding complexes were synthesized, characterized, and applied to the ethylene polymerization and E-MA copolymerization. In terms of ethylene polymerization, **NiC33 a–d** complexes exhibited high activities of up to 1.6×10^7 g of PE (mol of Ni)^{–1}h^{–1} (20 °C, 10 min) (Table 2). The synthesized polyethylene displayed high molecular weight (M_n) (up to 4.2×10^5 g/mol) with a molecular weight distribution of around 2.5. The structural variations **C33 a–e** had similar catalytic performance in ethylene polymerization. However, the polymer obtained from **C33e**-catalyzed polymerization was confirmed

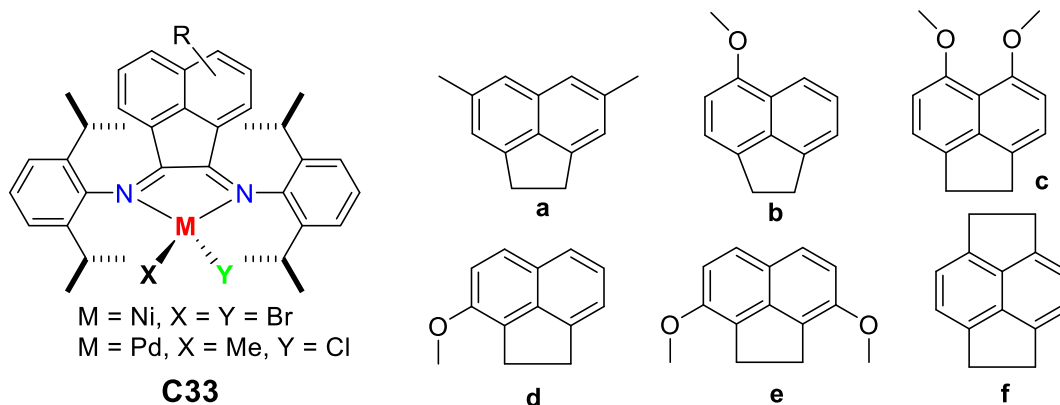


Fig. 21. Modified acenaphthyl substituted backbone modification.

to exhibit much higher molecular weight and lower branching density than polymers from other catalysts. Substituents on the ligand backbones of **PdC33 a-e** had a significant influence on their catalytic performance during ethylene polymerization and E-MA copolymerization. The polyethylene and E-MA copolymers produced by the **PdC33e** complex exhibited higher molecular weights than polymers from **PdC33 a-d**.

Along these lines, Zhu *et al.* reported the modification of acenaphthyl backbones on the α -diimine Ni complexes (**C33f** in Fig. 21), which has a similar structure as **C33a-e** complexes [119]. Experimental and computational studies were carried out to reveal and analyze the thermal stability of the proposed α -diimine Ni complex (**C33f**). Compared to the initially reported α -diimine Ni complexes (**A** in Fig. 1), the complex **C33f** presented higher activity and thermal stability at elevated temperatures (Table 2). It was found that the presence of ethylene evidently affected the conformation of the C1-N1-Ni-N2-C2 five-membered ring (where the nickel center is located) of **C33f**. According to calculations, differences in the decomposition energy between **C33f** and **A** in Fig. 1 were observed.

Zhang *et al.* explored the synthesis and characterization of new nickel bromide complexes containing the rigid bidentate bis(arylimino)camphane ligands with different *N*-aryl substituents (**C34** in Fig. 22) [120]. Upon activation with either MMAO or Me_2AlCl , the newly synthesized **NiC34** complexes exhibited high catalytic activities and thermal stabilities during ethylene polymerization (as high as up to 11.2×10^6 g PE (mol Ni) $^{-1}$ h $^{-1}$ (80 °C and 30 min)), producing PEs of high molecular weights (23.7×10^5 g mol $^{-1}$) and low PDI (1.6–2.6) (Table 2). In this catalytic system, the introduction of di(*p*-fluorophenyl)methyl on the *ortho*-position of *N*-aryl groups resulted in increasing of both the catalytic activity and the thermal stability of the corresponding

Ni complexes. The synthesized PEs were moderate to highly branched nature with the tunable branch contents governed by various ligand structures. The bulkiness of substituents in the ligand structure led to high molecular weight polymers with a low branching degree and limited types. The polymers produced with *ortho*-hydrogen **NiC34b**/ Me_2AlCl possessed the highest branching density with the unique terminal vinyl ($-\text{CH}=\text{CH}_2$) and internal vinylene ($-\text{CH}=\text{CH}-$) structures.

Long *et al.* proposed the newly synthesized α -diimine Ni complex containing dibenzobarrelene-bridged backbone (**C35** in Fig. 23) [121]. **C35** exhibited an exceptional catalytic behavior in ethylene polymerization. The DBB-bridged **C35** resulted in a steric hindrance around the cationic Ni center, decreasing catalytic deactivation and slowing the chain-walking process. Therefore, **C35** produced linear polyethylene in ethylene homopolymerization. **C35** Ni afforded a high molecular weight of polyethylenes (7.12×10^5 g/mol) with narrow distribution (1.18) and low branching densities (<1B/1000C) (Table 2). It also revealed a living polymerization behavior at room temperature, producing linear polyethylene with a high melting point ($T_m = 135$ °C) (Table 2). It facilitated the copolymerization of ethylene with the methyl 10-undecenoate to yield highly linear ester-functionalized polyethylene (T_m values at 128 °C and 1 mol% comonomer incorporation). In the presence of ester functional groups, the catalytic activity during copolymerization dropped by an order of magnitude. This was hypothetically attributed to the reversible coordination between the ester-functionalized co-monomer and the cationic Ni center.

Zhong *et al.* reported a series of α -diimine Ni and Pd complexes with the modifications of dibenzobarrelene-bridged backbone. (**C36a** in Fig. 23) [122]. These complexes also revealed high thermal stability and clear signs of living polymerization. **PdC36a** exhibited the ability for precision synthesis of functionalized copolymers by living ethylene copolymerization with various acrylate monomers (Table 2). The bulky enhancement of dibenzobarrelene backbone improved the insertion selectivity of methyl acrylate (MA) in a 2,1-insertion. This catalytic behavior prevented polar groups from poisoning the active **PdC36a** species. In this living chain-walking system, it was demonstrated that the composition, molecular weight, and branching topology of the copolymer could be controlled by the variation of the ethylene pressure. Based on backbone modifications of **C36a**, a series of novel dibenzobarrelene-derived α -diimine nickel complexes were also synthesized and applied in ethylene polymerization (**C36b-d** in Fig. 23). The increased steric effects on the ligand backbone and the repulsive interactions inhibited the *N*-aryl rotation of the α -diimine ligands and enhanced the thermal stability of the com-

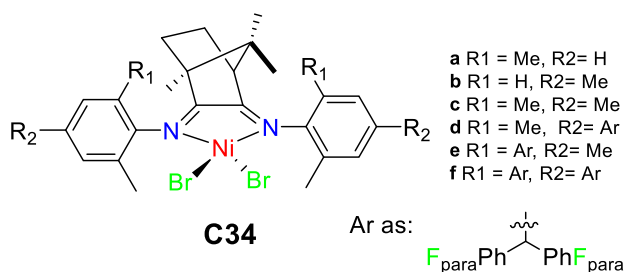


Fig. 22. Camphyl-bridged backbone modification.

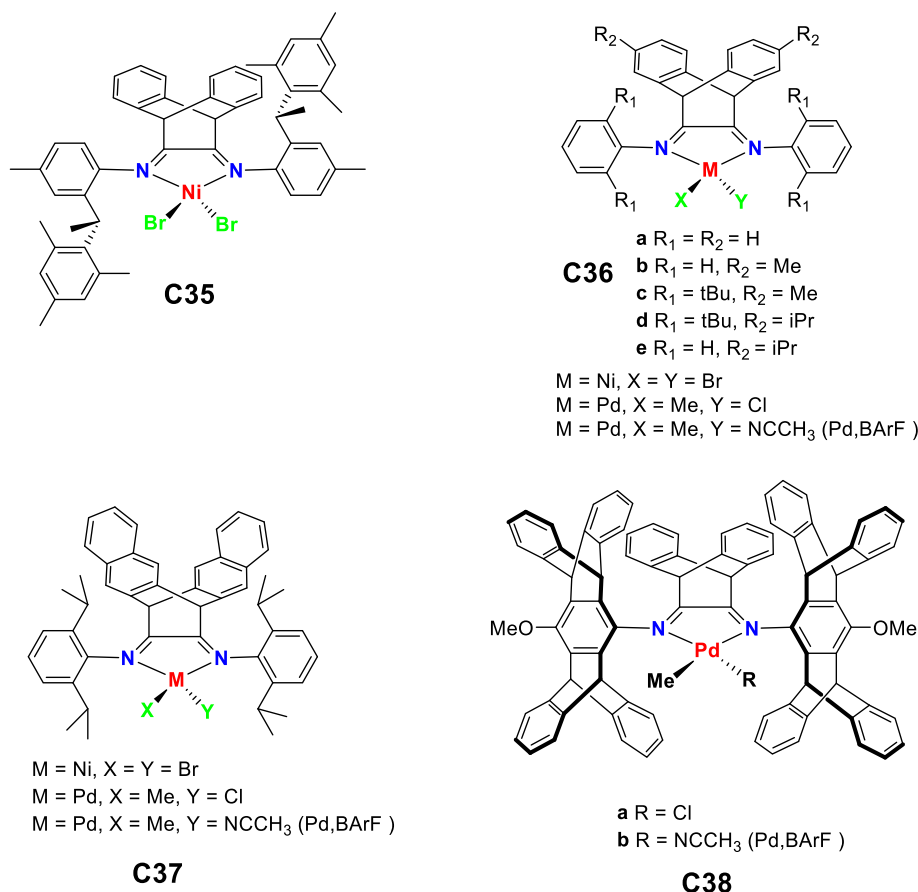


Fig. 23. Dibenzobarrelene-bridged backbone modification.

plexes. The living polymerization could be achieved at 80 °C. Bulky enhancement of dibenzobarrelene backbone also improved tolerance of Ni complexes towards the ethylene copolymerization with monomers containing polar groups. The living ethylene copolymerization with methyl 10-undecenoate was also carried out by the bulky **NiC36d**. **PdC36e** was applied in a precision synthesis of functionalized polymers by the living ethylene copolymerization with the variety of acrylate monomers [123]. The incorporation of the steric dibenzobarrelene backbone significantly improved the migratory-insertion selectivity of methyl acrylate (MA) in a 2,1-insertion manner. This bulk-enhanced strategy prevented the polar groups from poisoning palladium centers of the catalysts by a formation of the five-membered palladacycle intermediates **PdC36e** exhibited a living polymerization and good thermal stability (55 °C) during ethylene polymerization. Living ethylene copolymerization with MA monomer were also successfully achieved, which was in contrast to general knowledge that polar monomers poison the transition metal catalysts. **PdC36** was reported to perform the (co)polymerization of petroleum-based ethylene and bio-based furfuryl acrylate by *Du et al.* [124]. The cationic palladium catalyst exhibited higher thermal stability than the neutral chloromethyl palladium complex, while the later complex was more active at low temperature. The incorporation of *tert*-butyl on the dibenzobarrelene backbone improved the tolerance of the **PdC36** toward polar groups such as the incorporation of furyl groups into the polymer chain. Ethylene living (co)polymerization with the furfuryl acrylate (FA) catalyzed by **PdC36** was successfully carried out, which afforded copolymers with a uniform incorporation of FA. The mechanistic study indicated that FA was selectively inserted into the Pd–Me bond in a 2,1-insertion mode. There was

no interactions observed between the palladium center and the furyl ring. Then, the dinaphthobarrelene-based backbone of α -diimine Ni and Pd complexes was synthesized, providing three-dimensional confinement for ethylene (co)polymerization (**C37** in Fig. 23) [125]. These increased steric effects generated a 3D-confined space around the catalytic Ni and Pd centers, which strictly shielded the back and axial direction of the α -diimine Ni and Pd complexes. This confinement was assigned to the enhanced catalytic activity, thermal stability, and living fashion for ethylene polymerization (Table 2). The synthesized polyethylene possessed narrow molecular weight distribution (1.04–1.45). The steric accumulation effectively favored the ethylene copolymerization with polar monomers.

Zhang *et al.* proposed two types of dibenzobarrelene (backbone) and pentaptyceny (N-aryl) substituted α -diimine Pd complexes (**C38** in Fig. 23) [126]. Remarkably, the Pd complexes were active in a very broad range of temperatures (from 0 °C up to 130 °C). The Pd complexes allowed the synthesis of polyethylene with high molecular weight (around 10⁶ g/mol), see also Table 2. The microstructure analysis of the resulting polymers displayed highly methyl (220 Me/1000 C) branched features, which were close to the typical properties of commercial ethylene-propylene elastomers. In ethylene copolymerization with MA, elevating the reaction temperature from 30 °C to 90 °C gave rise to the increase in catalytic activity, molecular weight, and MA incorporation. This steric framework of **C38** exhibited an abundant chain-walking process, while the formation of branches in the polymer structure was only limited to methyl branches. The region-selectivity of acrylate insertion was characterized as 1,2-insertion due to the steric constraints.

Table 2Representative ethylene polymerization catalyzed by backbone modified α -diimine Ni and Pd catalysts.

C-Ni/Pd ^a	Co-cat.	T (°C)	t, min	Cat. ^b	P ^c	M _w ^d	PDI ^d	T _m (°C) ^e	B/1000C ^f	Ref.
C31e	EASC	40	30	4.41	10	0.21	2.10	99.9	32	[116]
C32-1R	Et ₂ AlCl	−10	30	0.52	1.2	0.50	1.27	71.4	41	[117]
C33c	MAO	20	10	16.1	9	0.18	2.18	49.0	91	[118]
C33f	MAO	60	30	0.61	1	0.17	1.80	123.0	–	[119]
C34e	Me ₂ AlCl	80	30	11.2	10	0.95	2.1	105.5	–	[120]
C35	MAO	−20	30	7 ^b	7	0.96	1.34	135.0	< 1	[121]
C36	Et ₂ AlCl	0	30	2.70	3	0.21	2.14	115.9	33	[122]
C37	Et ₂ AlCl	100	30	0.70	1.2	0.67	1.04	−13.3	95	[125]
C38	NaBARF	50	30	1.19	8	1.18	1.57	–	188	[126]

^a α -diimine Ni and Pd complexes.^b activity: $\times 10^6$ g of PE (mol of M)^{−1}h^{−1}.^c activity: Turnover frequency (TOF) = mol ethylene/(mol cat h), $\times 10^4$ h^{−1}.^d ethylene pressure in bar/atm.^e determined by GPC, $\times 10^6$ g/mol, PDI as polydispersity index.^f determined by DSC.^g branching density: Branches per 1000 carbon.

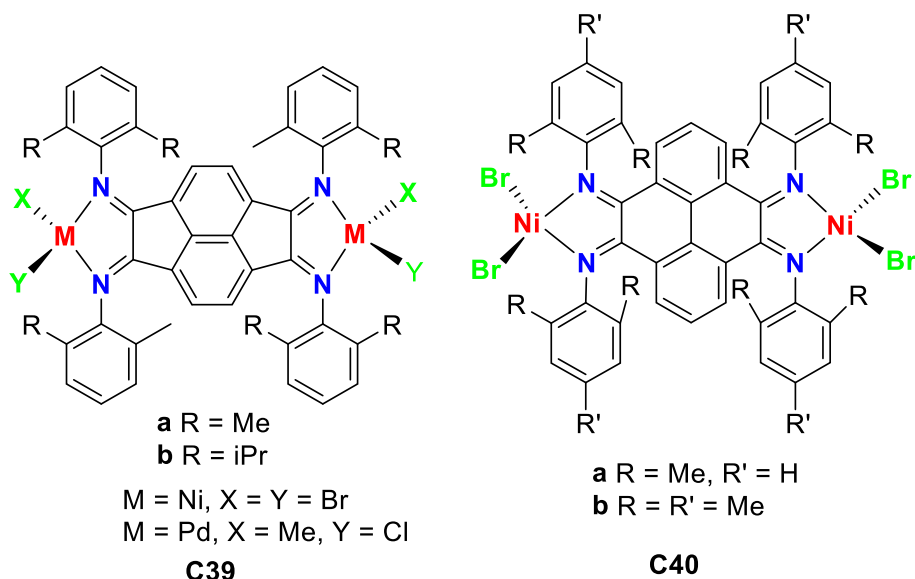
3.3. Binuclear complexes

A notable development of novel polymerization catalyst structures includes the integration of two active metal centers in asymmetric or symmetric binuclear complexes. It can pave the way to, for example, bimodal polymerization or synergistic activity enhancement. Table 3 summarizes these structures with the nomenclature **C39–C44**.

Zhu *et al.* reported a series of binuclear α -diimine Ni and Pd complexes containing conjugated backbones (**C39** in Fig. 24) [127]. Activated by MMAO, the catalytic activity of such complexes could reach up to 1.05×10^6 g of PE (mol of Ni)^{−1}h^{−1} (RT, 30 min) (Table 3). The activity of **NiC39b** is almost twice as high as the remaining complexes of this family, provided identical polymerization conditions. The binuclear **PdC39** produced polyethylene with bimodal features in GPC. This confirmed the simultaneous formation of two active species were in a binuclear catalyst system. The E/MA copolymerization was also investigated using the Pd complexes. The MA incorporation can be up to 2.36 mol% in the copolymerization catalyzed by **PdC39 b**.

Xing *et al.* reported a series of binuclear α -diimine Ni(II) complexes consisting of 4,5,9,10-tetra(arylimino)pyrenylidene-bridged ligands (**C40** in Fig. 24) [128]. To mediate ethylene polymerization, different parameters like type of cocatalysts, cocatalyst ratio, polymerization time, and temperature were varied to optimize the catalytic capacity of the binuclear Ni complexes. Both **NiC40 (a and b)** complexes exhibited high activities [1.5×10^6 g of PE (mol of Ni)^{−1}h^{−1}] (30 °C, 30 min) in the presence of either MAO or Me₂AlCl (Table 3). The Ni complexes exhibited a long time (60 min) of catalytic life when activated with MAO. The polyethylene obtained from the catalyzed polymerization revealed a minor amount of branches (7B/1000C). Compared to the analogous mononuclear complexes, these binuclear nickel complexes revealed no significant improvements in catalytic activity in ethylene polymerization.

Wang and Na *et al.* demonstrated the xanthene-, naphthalene- and biphenylene-bridged α -diimine binuclear Ni and Pd complexes **C41** (Fig. 25) [129,130]. These binuclear nickel complexes exhibit good thermal stability (stay active at 80 °C) during ethylene polymerization. They exhibited the catalytic activity up to 10^6 g of PE

**Fig. 24.** Conjugated backbone of binuclear complexes.

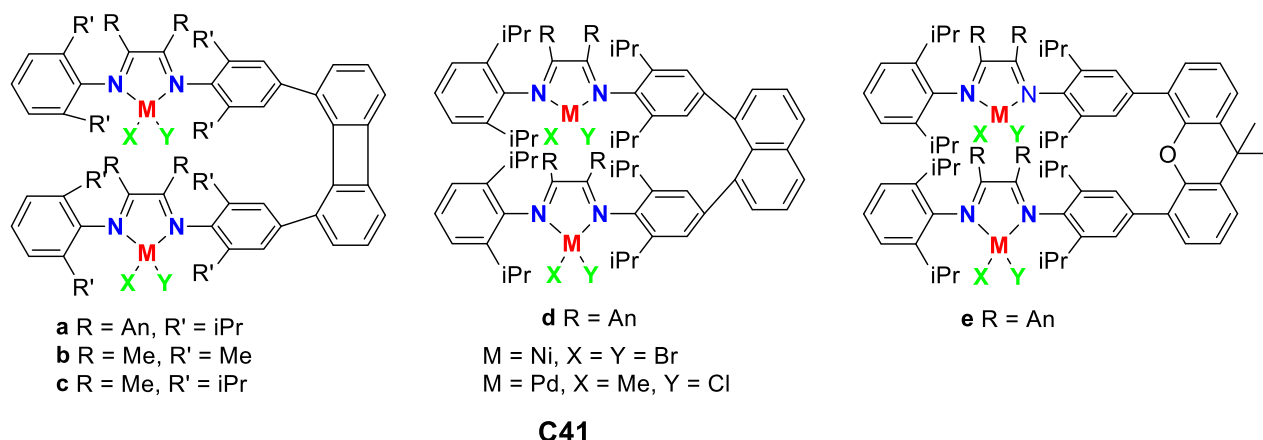


Fig. 25. Xanthene-, naphthalene- and biphenylene-bridged binuclear complexes.

(mol of Ni)⁻¹ (20 °C, 30 min) (Table 3). It was interesting to note that these binuclear Ni complexes exhibited higher activity and resulted in polymers with higher molecular weights than their mononuclear analogues. Polymers with a high molecular weight (M_n), narrow PDI and low branching density were obtained from these catalysts. These results indicated that the Ni-Ni cooperativity slowed the β -hydride elimination and related chain-walking process. In terms of Pd-catalyzed ethylene (co)polymerization, the Pd-Pd cooperation had a significant impact on catalytic behavior, especially for E-MA copolymerization. No MA incorporation was observed in the case of polymerization with the binuclear Pd complexes, while the mononuclear analogues enabled MA incorporation.

Kong *et al.* reported a series of methylene-bridged binuclear α -diimine Ni and Pd complexes **C42** (Fig. 26) [131]. Upon activation with Et₂AlCl or MAO, all the nickel complexes exhibited high activity toward ethylene polymerization [catalytic activity up to 7.86×10^6 g of PE (mol of Ni)⁻¹h⁻¹] (20 °C, 30 min). The resulting polymer displayed high melting points (T_m up to 130.9 °C) as well as high branching densities (151B/1000C) (Table 3). The binuclear Ni complexes exhibited a synergistic catalytic activity as compared to their mononuclear analogs. Furthermore, the synthesized polyethylene possessed a higher molecular weight and broader PDI (up to 4.8).

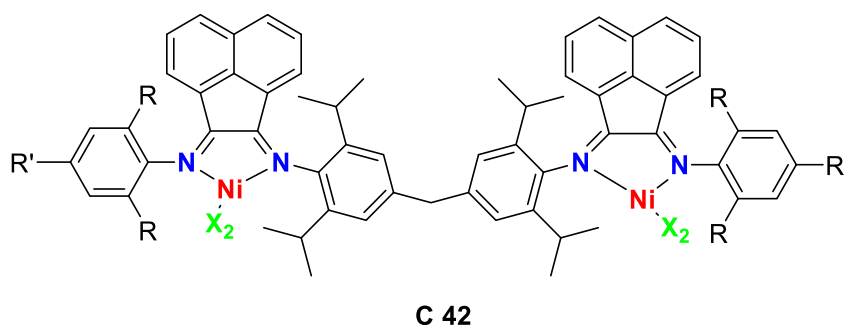


Fig. 26. Methylene-bridged binuclear complexes.

Khoshsefat *et al.* reported the aryl-bridged binuclear α -diimine Ni and Pd complexes **C43** (Fig. 27) [132]. Under the optimized conditions for ethylene polymerization ([Al]/[Ni] = 2000/1, 42 °C, 20 min), **C43d** reached its highest catalytic activity of 1.07×10^6 g of PE (mol of Ni)⁻¹h⁻¹ (42 °C, 20 min) (Table 3). Com-

pared to other Ni complexes, the polyethylene produced from **C43d** also processed the highest molecular weight with the broad molecular weight distribution (PDI = 17.8). The bulky *ortho*-substituents on *N*-aryl groups presented positive influences on the catalytic activity, molecular weights, and degree of branching, which was confirmed by the theoretical study as well.

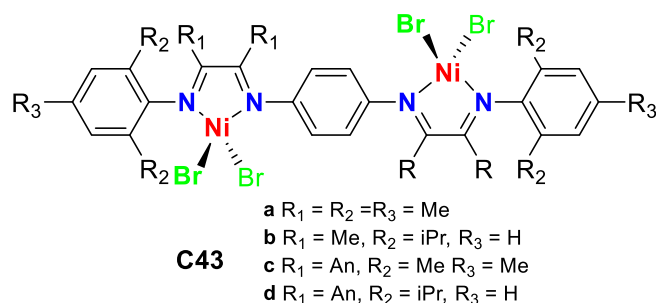


Fig. 27. Aryl-bridged binuclear complexes.

Takano *et al.* have developed a unique binuclear double-decker structure of α -diimine Pd complexes containing the macrocyclic ligands (**C44** in Fig. 28) [133–135]. In ethylene polymerization at

high temperatures (at 60 °C and 100 °C), **C44** exhibited more stability and higher activity than the mononuclear complexes (Table 3). The polyethylene formed by the binuclear catalyst **C44** possessed less branched density (33B/1000) than the mononuclear catalysts (110B/1000C). A longer catalytic lifetime for **C44** was also observed

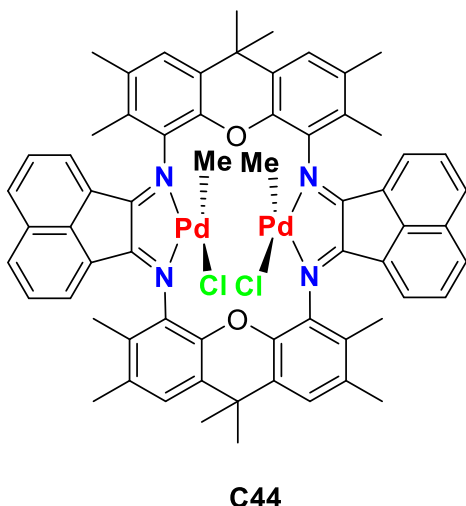


Fig. 28. Double-decker structured binuclear complexes.

as it was still active after 18 h. In E-MA copolymerization, the use of binuclear **C44** resulted in higher acrylate incorporation (5.2 mol %) in the copolymers than that formed by the mononuclear catalysts (1.1 mol %). NMR analysis confirmed branched structure for the E-MA copolymer. In E-AA (Acrylic Anhydride) copolymeriza-

tion, **C44** afforded copolymer containing a repeating unit of acrylic anhydride. High incorporation (up to 5.7 mol %) of cyclic and acyclic anhydride groups was evidenced in the main polymer chain, which was again much higher than the respective mononuclear complex (0.8 mol %).

3.4. Functional group modification

Zhong et al. developed α -diimine Pd complexes with two ferrocenyl units and applied them in the ethylene (co)polymerization (**C45** in Fig. 29) [136]. The two ferrocenyl groups were sequentially and stepwise oxidized, which increased the electron-withdrawing capacity of the α -diimine ligand. This stepwise redox control was applied to modify the catalytic properties of α -diimine Pd complexes during the ethylene homopolymerization and copolymerization with polar monomers (norbornene, methyl acrylate, and 5-norbornene-2-yl acetate). The catalytic activity decreased as the two ferrocenyl units become oxidized. It seemed that the rates of chain propagation and chain transfer were greatly affected by this stepwise redox-control strategy. The branching density of polyethylene was only slightly increased along with the oxidation, while the polymer microstructure and PDI was significantly controlled during these stepwise oxidation processes. The same ligands containing two ferrocene units was also applied to the synthesis of the α -diimine Ni complex. The oxidation process of the

Table 3
Representative ethylene polymerization catalyzed by binuclear α -diimine Ni and Pd catalysts.

C-Ni/Pd ^a	Co-cat.	T (°C)	t, min	Cat. ^b	P ^c	M _w ^d	PDI ^d	T _m (°C) ^e	B/1000C ^f	Ref.
C39	MMAO	RT	30	1.05	1	0.22	2.50	–	85	[127]
C40	MAO	30	30	1.50	10	0.23	2.20	131.4	8	[128]
C41	MAO	20	30	4.17	9	0.38	3.37	–	15	[129]
C42	Et ₂ AlCl	50	30	7.86	10	0.20	2.83	106.7	151	[131]
C43d	MAO	42	20	1.07	1.5	0.05	–	123.0	9.1	[132]
C44	NaBARf	40	1080	0.02	1	0.07	4.08	–	72	[133]

^a α -diimine Ni and Pd complexes.

^b activity: $\times 10^6$ g of PE (mol of M)⁻¹h⁻¹.

^c ethylene pressure in bar/atm.

^d determined by GPC, $\times 10^6$ g/mol, PDI as polydispersity index.

^e determined by DSC.

^f branching density: Branches per 1000 carbon.

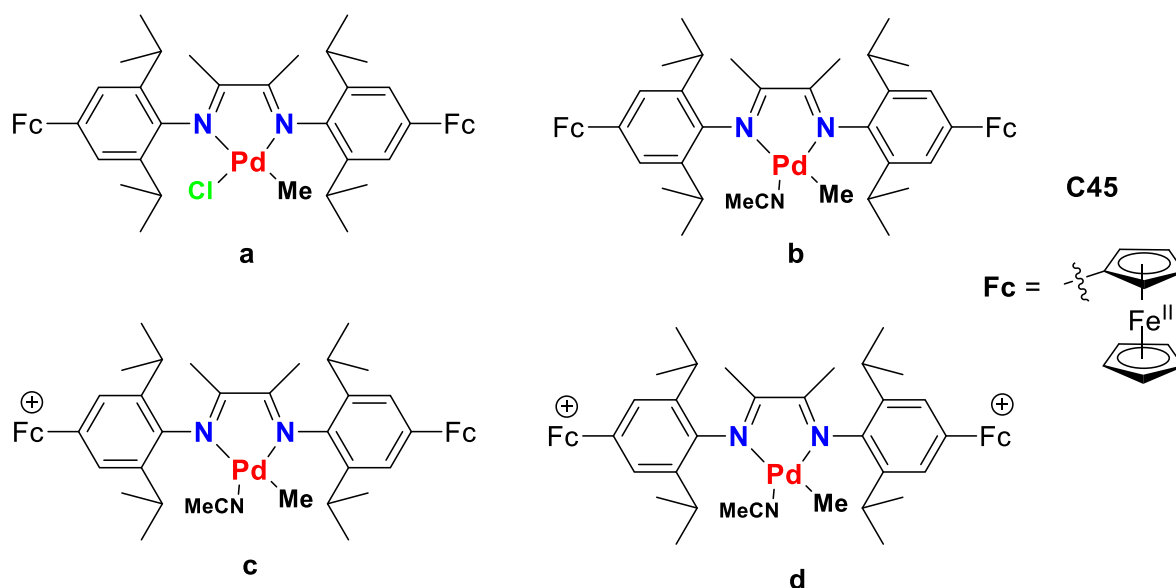


Fig. 29. Redox-controlled ethylene (co)polymerization catalyzed by α -diimine Pd complexes.

ferrocene groups did not alter the catalytic behavior of the corresponding Ni complex in ethylene polymerization. It was proposed that the reducing nature of the aluminum species (MAO) was too strong to carry out such stepwise redox-control strategy for Ni-catalyzed ethylene polymerization.

Peng *et al.* reported a new α -diimine Ni complex bearing azobenzene groups with photoresponsive properties toward ethylene (co)polymerization (**C46** in Fig. 30) [137]. The axial steric environment of the metal center was directly influenced by the light-induced trans-cis isomerization. UV light can tune the properties of the ligand structure and therefore the catalytic behavior of the α -diimine Ni complexes for ethylene (co)polymerization. This light-induced control increased the polymer molecular weight and decreased the catalytic activity and the polymer branching density (Table 4). The authors suggested the incorporation of the photo-responsive functional units could induce even more dramatic changes in the electronic and steric coordination environments around the catalytic metal center.

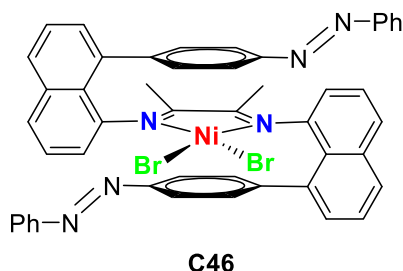


Fig. 30. Photochemistry for ethylene (co)polymerization catalyzed by α -diimine Ni complexes.

Metal-metal cooperation and synergistic effects have been extensively explored in ethylene polymerization, like the synthesis and application of the binuclear transition-metal catalysts. Contrary to this strategy, Wang *et al.* proposed a supramolecular chemistry strategy which was carried out to construct multinuclear catalysts for ethylene (co)polymerization. A new series of α -diimine Pd complexes was designed and synthesized with the urea-functional groups (H and *N*-methylated counterparts) (**C47** in Fig. 31)[138]. The experimental results indicate that self-assembly of Pd complexes took place via the urea-based hydrogen bonding interactions, which was evidenced from the Fourier transform infrared (FTIR) spectroscopy. During ethylene polymerization and copolymerization with MA, the catalytic activity and polymer properties such as molecular weight, PDI, branching density, comonomer incorporation of the (co)polymer were modified by the various catalyst concentration, ligand structures, and reaction conditions. In order to further explore the supramolecular-induced self-assembly effects, the photo-sensitive azobenzene group was incorporated in the urea-functionalized α -diimine Pd complexes. This work indeed showed the presence of photosensitive functional group in the nickel complex influenced the microstructure of the polyethylene.

The aliphatic hydrocarbon solvents (hexane and heptane) were widely applied in the industrial research for ethylene polymerization, while the academic researchers predominantly worked on properties of the catalyst in aromatic solvents (toluene). In order to bridge this gap between academic studies to practical applications, Chen *et al.* designed the new α -diimine Ni complex with the diaryl-methyl aniline bearing eight *tert*-butyl groups (**C48** in Fig. 32) [139]. The incorporation of the multiple *tert*-butyl substituents in the diaryl-methyl moiety increased both the ligand's steric and electronic-donating ability. It resulted in the enhancement of the catalyst stability and polymer molecular weight in ethylene polymerization. The presence of multiple *tert*-butyl groups enabled solubility of the metal complexes in aliphatic hydrocarbon solvents, leading to similar polymerization properties compared to the aromatic solvents. The incorporation of *tert*-butyl substituent in the ligands improves the solubility of the Ni complexes in typical polymerization solvents, which improves its application potential.

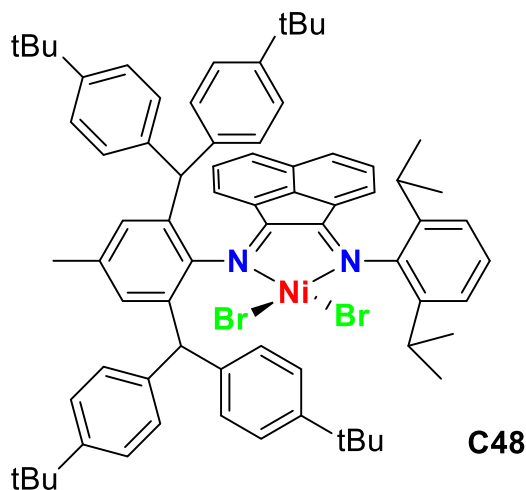


Fig. 32. Ethylene (co)polymerization in aliphatic hydrocarbon solvents using *tert*-butyl substituted α -diimine Ni complex.

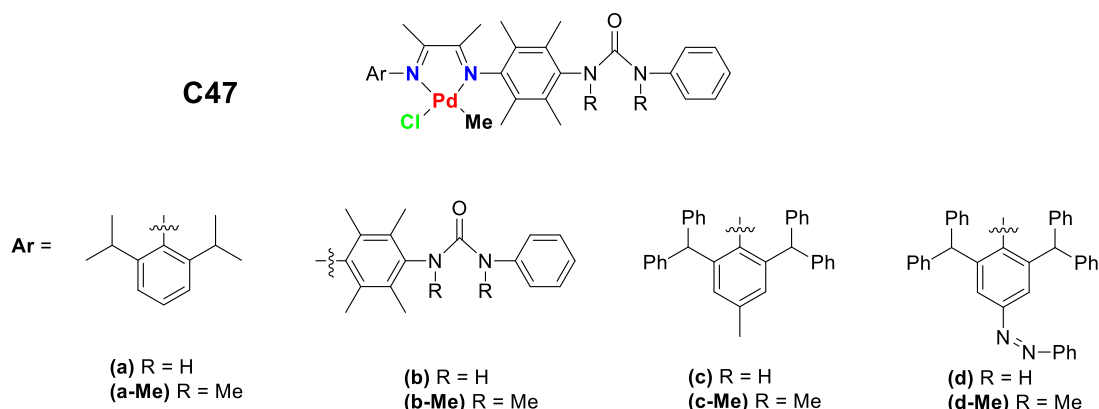


Fig. 31. Supramolecular chemistry and photochemistry with α -diimine Pd catalyzed ethylene polymerization.

Gong *et al.* developed a new series of acenaphthene-based sterically hindered α -diimine Pd complexes bearing bulky diarylmethyl moiety for ethylene (co)polymerization (**C49** in Fig. 33) [140]. The π - π interaction between the acenaphthene moiety and the phenyl of diarylmethyl moiety was suggested to occur. The π - π interaction was considered as the capacity to freeze the *N*-aryl-bond rotation at room temperature, resulting in the enhancement of the axial steric bulk and thus resulting in a low branching density of the polyethylene. The highest catalytic activity after 60 min [6.73×10^4 g of PE (mol of Pd) $^{-1}$ h $^{-1}$] was achieved at 60 °C. At high temperature, the effects of the π - π interaction were decreased while the branching densities of polyethylene were significantly increased. Consequently, the branching density and the microstructure of the polyethylene were modified by the various reaction conditions. In terms of the ethylene copolymerization with polar monomers, moderate catalytic activities (up to 6.8×10^4 g of copolymer (mol of Pd) $^{-1}$ h $^{-1}$), high molecular weight copolymers (M_n up to 4.8×10^5 g mol $^{-1}$) and low incorporation ratios of polar monomers (up to 2.12 %) were observed. This work also indicated that the π - π interaction effect played a critical role in copolymerization as well as ethylene homopolymerization.

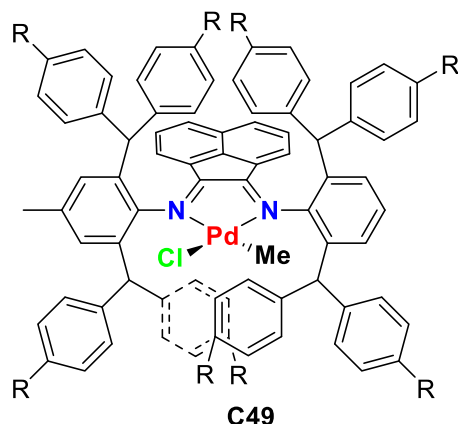


Fig. 33. π - π Interaction effect in ethylene (co)polymerization with α -diimine Pd complexes.

Zhong *et al.* proposed a series of α -diimine Ni and Pd complexes with electron-donating/withdrawing groups on the dibenzobarrelene backbone for ethylene polymerization (**C50** in Fig. 34) [39,141]. The electronic effects from the remote substitutions on the backbones influenced the catalytic performance of the corresponding Ni complexes. The electron-withdrawing halogens

enhanced catalytic activity and polymer molecular weight, while electron-donating methoxy groups led to a decrease. **C50** displayed the highest activity [5.6×10^5 g of PE (mol of Ni) $^{-1}$ h $^{-1}$ (50 °C, 30 min)] and produced the highest molecular weight polyethylene (3.3×10^5 g/mol) (Table 4). Intra-ligand hydrogen bonding interactions (C—H...OMe) were observed in the **C50a**. The weak and non-covalent interactions enhanced the catalyst thermal stability and brought about a living ethylene polymerization at high temperatures (80 °C) via inhibiting rotation of the *N*-aryl bonds. The dibenzobarrelene-based α -diimine Pd complexes (**PdC50**) exhibited the thermally robust characteristics for ethylene polymerization, due to the cooperative effect of hydrogen bonding interactions, electronic modification, and steric modification. The chloro-substituted Pd precatalyst presented the best thermal robustness for ethylene polymerization. In terms of the copolymerization with polar monomers, methoxy-substituted Pd precatalyst showed the most excellent tolerance toward both high temperature and polar groups. High MA incorporation (up to 9.5 mol%) can be achieved via the ethylene copolymerization with methyl acrylate (MA) at 80 °C. Compared to the previous strategies on weak noncovalent interactions in catalyzed ethylene polymerization, these hydrogen bonding interactions provided a fundamentally new approach in enhancing thermal stability of the α -diimine Ni and Pd complexes.

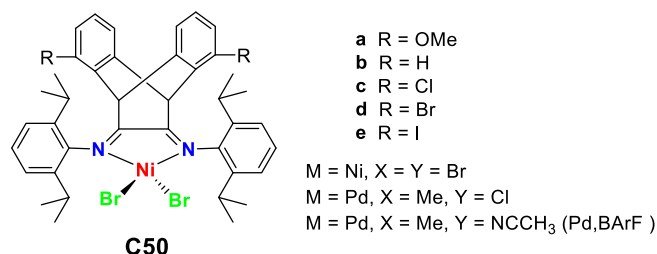


Fig. 34. Hydrogen bonding interaction in ethylene polymerization with α -diimine Ni complexes.

Zheng *et al.* investigated the α -diimine Ni complexes with bulky 8-*p*-tolynaphthylamine and dibenzo-/dinaphthobarrelene backbones for ethylene polymerization (**C51** in Fig. 35) [142]. The weak Ni-phenyl interactions were considered as confining elements of the α -diimine Ni complexes. The interactions thus promoted the acceleration of the chain-growth process. **51Nia** and **51Nib** exhibited enhanced thermal stabilities and activities [1.39×10^6 g of PE (mol of Ni) $^{-1}$ h $^{-1}$ (80 °C, 30 min)]. The synthesized PE was charac-

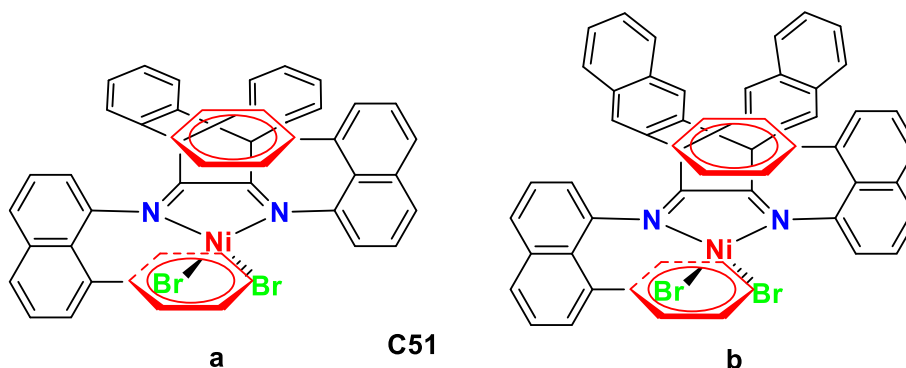


Fig. 35. Square-planar geometries and Ni-phenyl interactions in ethylene (co)polymerizations with α -diimine Ni complexes.

terized as a linear semi-crystalline polymer. The combined experimental and theoretical study demonstrated the Ni-phenyl interactions decreased PE branching density in catalyzed ethylene polymerization. This work addressed the effects of Ni-phenyl interaction induced confinement, which provided an alternative strategy to prepare linear PE. Ni-phenyl interactions were also observed to promote E-MA copolymerization, where the MA incorporation was confirmed as 2.1 mol %.

Wang et al. reported a new family of α -diimine Ni and Pd complexes bearing axially bulky terphenyl and equatorial bulky dibenzobarrelene groups (**C52** in Fig. 36) [143,144]. Due to the presence of bulky groups, chain transfer was limited in the ethylene polymerization. These novel nickel complexes yielded polyethylenes of ultrahigh molecular weights (M_w as high as 1.74×10^6 g/mol). Meanwhile, the use of the unsymmetrical skeleton with both bulky terphenyl group and less bulky aniline group resulted in a high catalytic activity as 1.52×10^7 g of PE (mol of Ni) $^{-1}$ h $^{-1}$ (20 °C, 10 min) (Table 4). The incorporation of the electrowithdrawing trifluoromethyl group into the terphenyl moiety clearly gave rise to H-F interactions between the *N*-terphenyl/aniliny group and the dibenzobarrelene backbone. This interaction efficiently suppressed the rotation of the *N*-terphenyl/aniliny moiety, leading to relatively higher thermostability. The α -olefin polymerization studies revealed quite a large amount of ω ,1-enchainments. Due to the axial and equatorial bulkiness and the weak H-F interactions, the deactivation of the active species at high temperatures was relatively reduced. At 80–140 °C, the Pd complexes efficiently catalyzed norbornene polymerizations with high catalytic activity (up to 5.65×10^7 g of PNB (mol of Ni) $^{-1}$ h $^{-1}$) and yielding high molecular weights of PNB (up to 37.2×10^4 g/mol). Moreover, the Pd complexes could successfully promote the norbornene copolymerization with NB-MA, achieving moderate catalytic activities [10^4 g of copolymer (mol of Pd) $^{-1}$ h $^{-1}$ at 80 °C (60 min)].

4. Heterogeneous polymerization

The immobilization of the catalytic metal center onto inorganic supports is a crucial step for gas and slurry-phase polymerization in the industry [145–147]. Compared to the common supported heterogeneous catalyst, α -diimine Ni and Pd complexes provided much higher catalytic activity up to 10^7 g of PE (mol of Ni) $^{-1}$ h $^{-1}$ (or even higher) for ethylene polymerization. Molecular weight and molecular weight distribution of polyethylene could reasonably be controlled and modified using α -diimine Ni and Pd complexes, which gave us the chance to produce high-value polymers rather than the lower-quality polyolefins (broad dispersity and low molecular weight) from Ziegler-Natta systems [148,149]. Therefore, heterogenization of α -diimine Ni and Pd complexes provided a promising opportunity for a convenient “drop-in” approach for novel catalytic solutions in industrial-scale production processes. However, previous academic studies on α -diimine Ni and Pd complexes were mainly focused on homogeneous systems [44–150]. In industry, however, the heterogeneous polymerization is still the predominant polyethylene synthesis method. Consequently, it is rare to find commercial applications of α -diimine Ni and Pd complexes for olefin polymerization [151]. This section summarizes the various recently reported immobilizing methods (either physisorption or chemisorption) for α -diimine Ni and Pd complexes. Successful immobilization of the well-defined, single-site catalysts such as α -diimine Ni and Pd complexes on inorganic supports would definitely be the best solutions for their industrial applications. Heterogeneous catalysis has the advantage over the homogeneous catalysis in terms of separating the catalyst from the polymer during recycling, which is considered as the key drawback of homogeneous catalysis [44]. This strategy has been the most efficient tool to establish a heterogeneous platform for olefin polymerization.

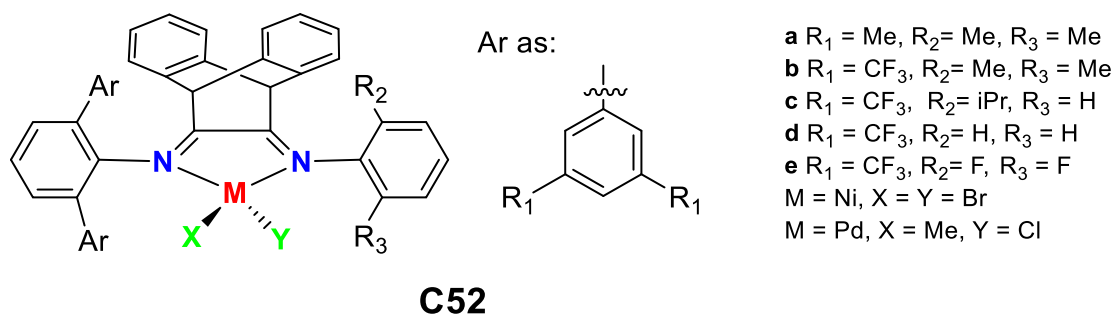


Fig. 36. H···F interactions in ethylene and norbornene polymerizations with α -diimine Ni and Pd complexes.

Table 4

Representative ethylene polymerization catalyzed by α -diimine Ni and Pd catalysts with functional group modification.

C-Ni/Pd ^a	Co-cat.	T (°C)	t, min	Cat. ^b	P ^c	M _w ^d	PDI ^d	T _m (°C) ^e	B/1000C ^f	Ref.
C45c	NaBARf	40	180	0.074	8	0.40	2.31	–	89	[136]
C46	MAO	0	30	3.34	8	1.34	1.52	114.4	48	[137]
C47c	NaBARf	25	180	0.104	8	0.31	1.34	–	100	[138]
C48	Et ₂ AlCl	25	3	34.4	8	1.73	2.18	78.33	53	[139]
C49c	NaBARf	60	60	0.67	8	0.77	2.58	65	51	[140]
C50e	Et ₂ AlCl	50	30	0.56	1.2	0.33	1.07	–	104	[39]
C51a	Et ₂ AlCl	80	30	1.39	20	0.76	1.82	90	33	[142]
C52a	MAO	20	10	15.2	10	1.75	1.66	103.6	29.3	[143]

^a α -diimine Ni and Pd complexes.

^b activity: $\times 10^6$ g of PE (mol of M) $^{-1}$ h $^{-1}$.

^c ethylene pressure in bar/atm.

^d determined by GPC, $\times 10^6$ g/mol, PDI as polydispersity index.

^e determined by DSC.

^f branching density: Branches per 1000 carbon.

The chemisorption methods for α -diimine Ni and Pd complexes could be classified based on the types of immobilization techniques: i.e i) covalent attachment or ii) surface-bound anions as shown conceptually in Fig. 37. The former method involved the covalent bonding between the silica supports and α -diimine Ni and Pd complexes, with the help of a linker (R in Fig. 37). The latter approach involves the treatment of the silica particles with cocatalysts (MAO, TAM, or others) to form surface-bound Al compounds. Then, the Al compounds served as the initiator to convert the complexes into active cationic metal-alkyl complexes. In this way, the complex was successfully immobilized onto the support particles through the ionic attraction to the surface-bound anions (electrostatic interactions) [150].

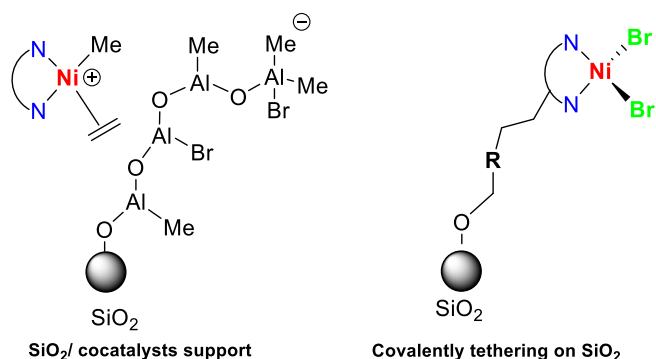


Fig. 37. Graphical concept of supported α -diimine Ni and Pd complexes on SiO_2 nanoparticles.

Wegner et al. has developed an efficient synthetic strategy for novel 2,5- and 2,6-phenyl substituted α -diimine Ni complexes (C53 in Fig. 38) [152]. The Ni complexes were directly supported during catalyst synthesis, without any further chemical links. These surface-bound catalysts were applied for ethylene polymerization in the gas phase. Unsupported C53a and C53b Ni complexes were benchmarked in the homogeneous solution for the comparison study, also with the gas-phase polymerization. The supported catalysts presented strong chemical stability. Even after several

months, no decomposition was observed. The supported catalysts exhibited moderate activities in ethylene polymerization, which was up to 1.36×10^5 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$ (30 °C, 60 min) (Table 5). The produced polyethylene exhibited the features typical for α -diimine Ni catalyst; i.e. ranging from HDPE to LLDPE with narrow PDI and low branching densities. In general, polyethylene produced in the gas phase exhibited higher molecular weights than those obtained from solution polymerization. The growth of single polyethylene particles was investigated in gas-phase polymerization using video microscopy. All the Ni complexes exhibited strong tolerance towards hydrogen additions during ethylene polymerization.

Huang et al. has developed an ionic immobilized C19d Ni complex (Fig. 39) onto the silica via different Al organic compounds (Et_3Al and Et_2AlCl) (C19d@ SiO_2). The immobilized Ni complexes displayed moderate activities [0.68×10^6 g of PE (mol of Ni) $^{-1}\text{h}^{-1}$] (50 °C, 60 min) towards ethylene polymerization, initiated by the co-catalyst either $i\text{Bu}_3\text{Al}$ or Et_2AlCl [153]. The synthesized polyethylene was characterized as medium branching densities (30–50 $\text{CH}_3/1000\text{C}$), ultrahigh molecular weights (up to 2.2×10^6 g/mol), and narrow molecular weight distributions (2.1–2.4) (Table 5). The supported nickel complexes produced spherical particles of polyethylene upon slurry-phase polymerization, while noteworthy, there was no reactor fouling.

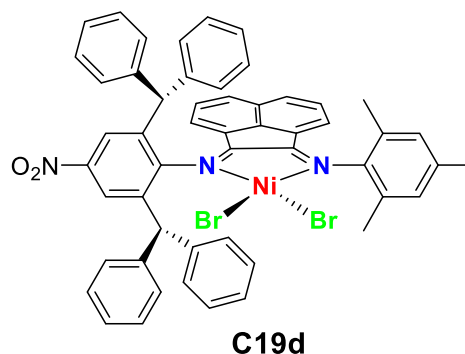


Fig. 39. Typical Ni complexes supported on silica modified by different aluminum compounds.

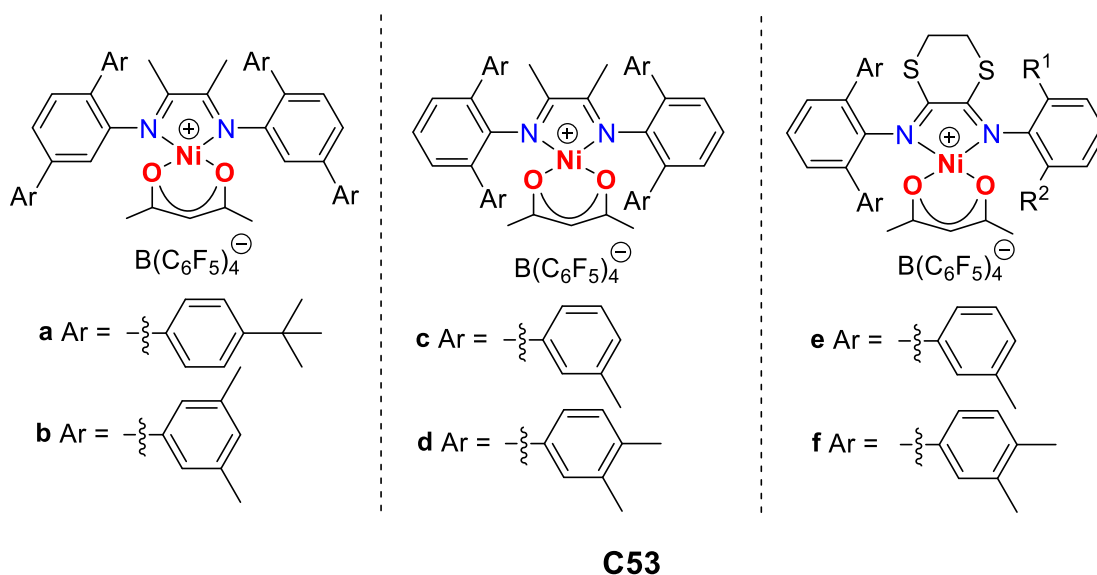


Fig. 38. Gas-phase polymerization of ethylene with directly supported complexes.

Based on the initial complex **A**, *Fevero et al.* recently developed a series of functionalized α -diimine Ni complexes with covalent tethers (**C54–58** in Fig. 40) [154]. The Ni complexes were covalently attached to the mesoporous silica (MCM-41) which were applied in ethylene heterogeneous polymerization. The Ni precatalysts were directly attached as the single precursor (**C56** and **C57**) or a binary precursor (**C58**) to the TMA treated silica. Under optimized conditions, the binary catalysts exhibited similar catalytic performance as the homogeneous catalysts [as high as 3.97×10^6 g of PE (mol of Ni) $^{-1}$ h $^{-1}$] (30 °C, 20 min) (Table 5). The analytical evidence from GPC and the thermal test indicated that both catalysts of the binary precursor were highly active during ethylene polymerization. **C56** catalysts delivered high linear polymers while the **C55** and **C57** yielded branched polymers. The use of binary **C58** catalyst resulted in polymers as the different functions, which was assumed to be due to the polymers' mixture. The functionalized tethers and covalent attachment both from the backbone and *N*-aryl groups were proven as a successful strategy to immobilize the α -diimine Ni(II) complexes on the solid support.

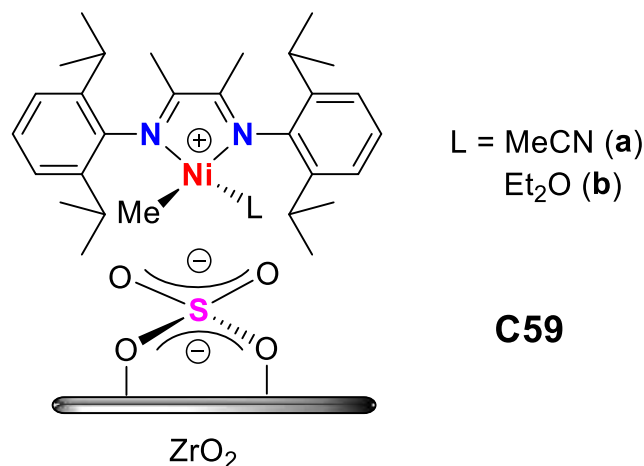


Fig. 41. α -Diimine Ni(II) complex supported on sulfated zirconia.

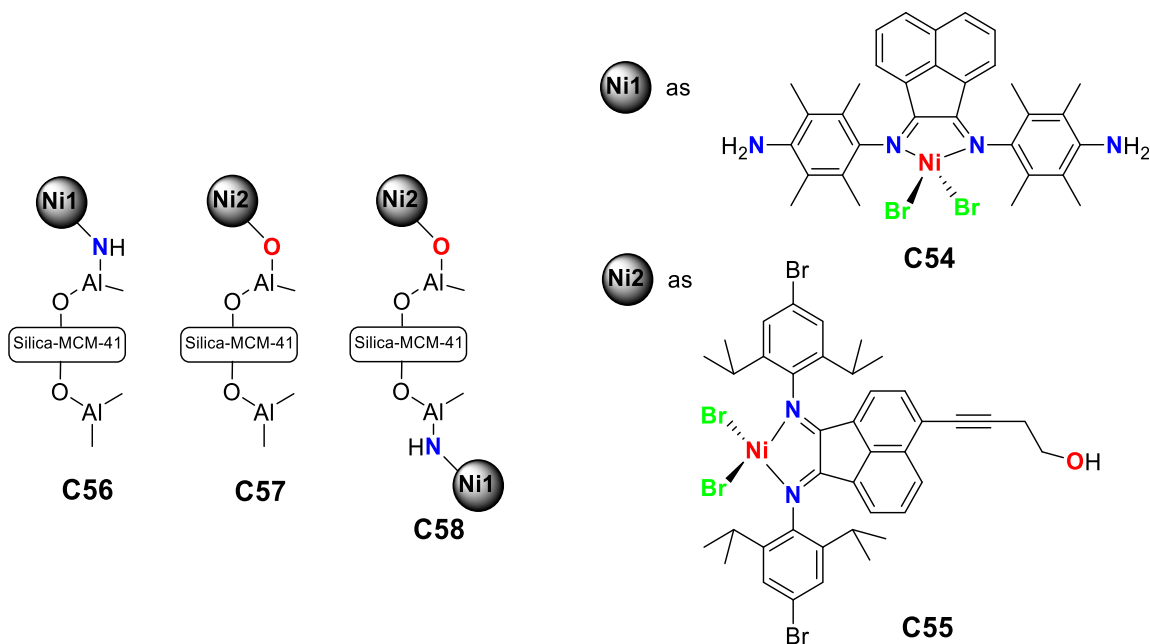


Fig. 40. Synthesis of the tethered Ni complexes on silica.

Tafazolian et al. reported a unique form of immobilizing the α -diimine Ni(II) complex on the inorganic ZrO₂ [155]. The calcined ZrO₂ and dilute sulfuric acid solution formed firstly the sulfated zirconium oxide (SZO) sites, which contained Brønsted acids. These active sites allowed the ionic support of α -diimine Ni complex on the ZrO₂, which was already partially dehydroxylated at 300 °C. In the MeCN/Et₂O solution, the immobilizing reaction took place between the (α -diimine)NiMe₂ complex and SZO, generating the ionic support and methane (**C59** in Fig. 41). Under 45-psi ethylene pressure, **C59b** polymerized ethylene monomer in toluene with the TOF of 21000 h $^{-1}$ at 40 °C (15 min) (Table 5). The high molecular-weight polyethylenes were produced in catalyzed polymerization ($M_n = 1.53 \times 10^5$ g/mol). The polymers exhibited moderate branching as 71B/1000C with a narrow PDI around 1.8. The elevated temperatures gave rise to a decrease in catalytic activities, polymer molecular weights, and molecular weight distribution. A steady decrease in the catalytic activity was observed with the increased reaction time in slurry-phase polymerization. Ethylene copolymer-

ization with 10-undecenoate was also performed in this study. Compared to the polyethylenes, the synthesized copolymers presented a moderate molecular weight ($M_n = 2.97 \times 10^4$ g/mol) with broad dispersity (PDI = 5.17).

Bahuleyan et al. have reported a leaching-free strategy to directly support the α -diimine Ni complexes on nonporous silica (**C60** and **C61** in Fig. 42) [156]. This method avoids any tedious process, such as the chemical and thermal treatments of the silica substrate. The reactive amino groups on the α -diimine Ni complex provided the functionality to prepare the covalently supported catalysts. Firstly, amino-functionalized ligands reacted with the organosilane, 3-(triethoxy-silyl)propylisocyanate, which played the role of linkers on the ligands. Using the Stober method, the silica-supported ligands or complexes (after metalation with (DME)NiBr₂) were prepared by the reaction between linkers with SiO₂. Instead of the MAO-supported forms, the catalytic activity of the supported systems could be up to 10⁶ g of PE (mol of Ni) $^{-1}$ bar $^{-1}$ h $^{-1}$ (30 °C, 60 min) with activation of a very small amount

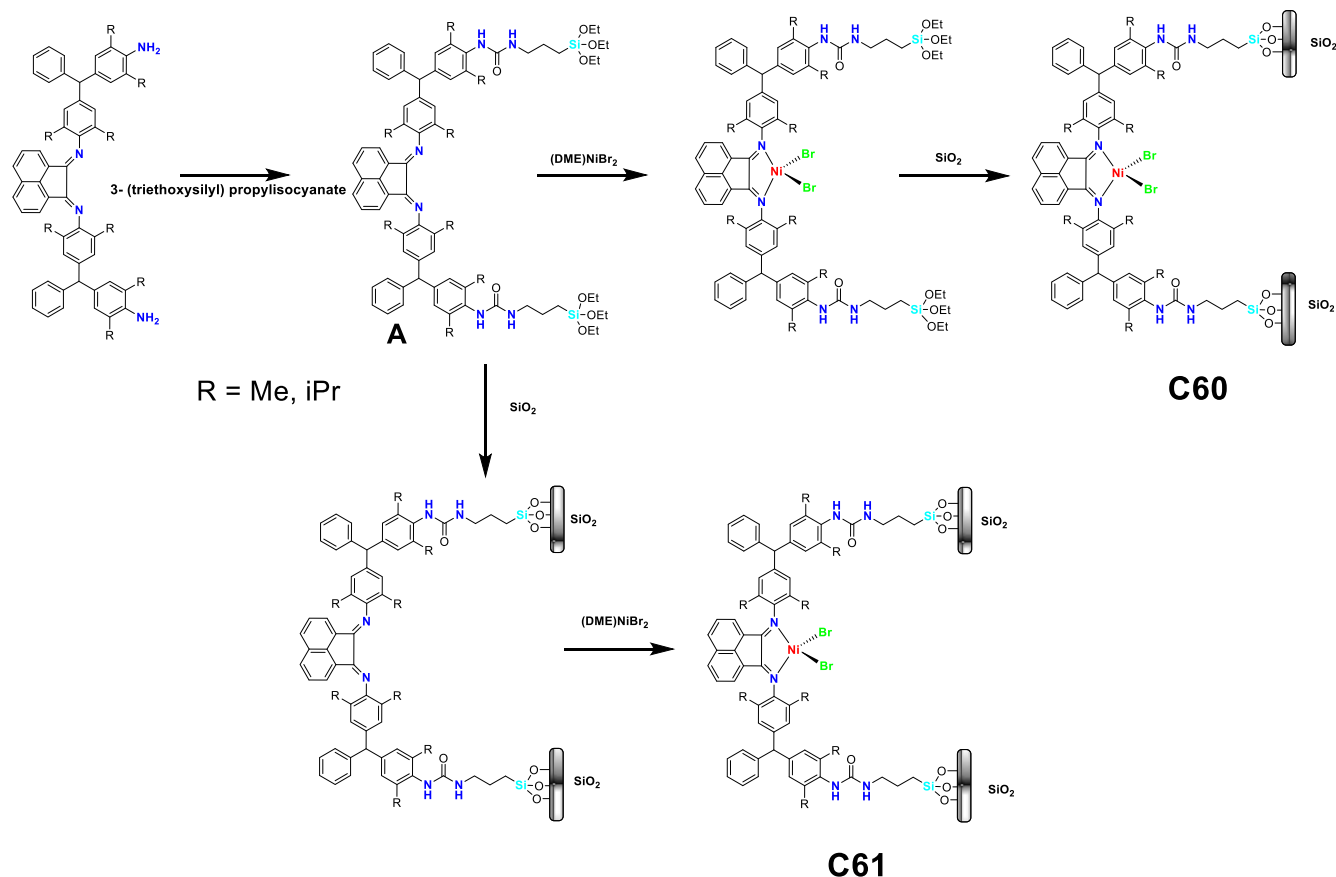


Fig. 42. Synthesis of tethered α -diimine Ni complex on the SiO_2 .

of aluminum compounds (Al/Ni 100) like EASC, MeAlCl_2 , and $\text{Et}_2\text{-AlCl}$ (Table 5). No visible leaching from the active metal centers or pollution of the reactor was observed in the heterogeneous ethylene polymerizations. The types of cocatalysts, catalytic activities, and metal loadings were considered the main factors influencing the morphology of polyethylenes. Electron microscopic investigations indicated a fibrous architecture for the polymers.

mechanical and other properties of the polymers [157]. Due to the chain walking process, α -diimine Ni complexes produced mainly branched polymers using only ethylene as the monomer feedstock [158,159]. The structural modifications on the ligand backbone and *N*-aryl substituents of the α -diimine Ni complexes played a crucial role in controlling the chain-walking behavior, which had a significant influence on the polymeric branching den-

Table 5
Representative ethylene polymerization catalyzed by heterogeneous α -diimine Ni and Pd catalysts.

C-Ni ^a	Co-cat.	T (°C)	t, min	Cat. ^b	P(bar) ^c	M_w ^d	PDI ^d	T_m (°C) ^e	B/1000C ^f	Ref.
C53a	TMA	30	60	0.14	10	2.3	1.6	126.7	8	[152]
C19d@SiO₂	iBu ₃ Al	30	60	0.68	10	2.2	–	–	44	[153]
C57	EASC	30	20	3.97	4	–	–	117	–	[154]
C59b	–	40	15	2.10 ^{b*}	3	0.28	1.8	–	71	[155]
C61	EASC	30	60	1.05	5.5	0.23	3.3	131	13	[156]

^a α -diimine Ni and Pd complexes.

^b activity: $\times 10^6$ g of PE (mol of Ni)^{–1}h^{–1}.

^{b*} activity: Turnover frequency (TOF) = mol ethylene/(mol cat h), $\times 10^4$ h^{–1}.

^c ethylene pressure in bar.

^d determined by GPC, $\times 10^6$ g/mol, PDI as polydispersity index.

^e determined by DSC.

^f branching density: Branches per 1000 carbon.

5. Polymer properties

In the field of coordination-insertion polymerization catalyzed by the late-transition metal complexes, the polymeric microstructures are largely governed by catalyst structures and reaction conditions. The control over microstructure has a direct influence on

sities. The branching nature of the polymers were determined by the high temperature ¹H and ¹³C NMR, where the branching degree (per 1000C) were calculated (Fig. 43) [54,107,160]. In the high temperature ¹³C NMR spectra, the types and percentage of the various branches could be characterized clearly, like methyl, ethyl, propyl, butyl, amyl and even longer chains. These branched polymers are

part of the polyolefin thermoplastic elastomers (P-TPE) [157]. Compared to the thermoplastics polymers (like HDPE), a low Young's modulus, high elongation at break, and high elastic recovery is typical for P-TPE-type materials. The stress-strain curves indicated mechanical properties like tensile strength and elongation at break that are typical for P-TPE materials (Fig. 44A). The elastic recovery of the P-TPE materials was also confirmed (Fig. 44B) [82]. For example, Sui *et al.* synthesized a series of the elastic polyethylenes catalyzed by the unsymmetrical α -diimine Pd complexes, which displayed very nice mechanical properties [160]. High tensile strengths (18 MPa) and great elastic properties, like elongation at break close to 500 %, were observed. The molecular weight and broad PDI were considered as the main factor, influencing the mechanical performance of the polymers. In 2017, Lian *et al.* reported the synthesis of PE-based TPEs catalyzed by the α -diimine Ni complexes [82]. The tensile strength (3 to 28 MPa) and elongation-at-break (300 % to 1800 %) values of these

polymers could be modified by different Ni complexes and polymerization conditions. An exceptional elastic recovery as high as 1605 % was noted. One year later, Fang *et al.* developed the newly synthesized elastomeric materials via ethylene polymerization, which exhibited good tensile strength ranging from 7.4 to 16.3 MPa and elongation-at-break values ranging from 450 % to 700 % [158]. Notably, the mechanical properties of the polymers were significantly influenced by their molecular weights and branching densities. In addition, an elastic recovery up to the strain recovery values of 83 % was observed. More recently, Liu *et al.* reported a series of highly branched polyethylene (161 branches/1000C) catalyzed by the trifluoromethoxy-substituted α -diimine Ni catalysts [107]. The lowest tensile strength was up to 3.3 MPa, while the highest elongation at break was observed as 984 %. The elastic recovery were determined as 71 %. The molecular weight, crystallinity, and the alkyl-branching architectures significantly influenced the tensile strength of these polymers. The distinctive properties of the produced polymers was believed to be the promising alternatives to the commercial thermoplastic elastomers.

Besides the unique elastic properties, the copolymers incorporated with the polar monomers catalyzed by the α -diimine Ni and Pd complexes exhibited remarkable hydrophilicity (Fig. 45) [79]. This hydrophilicity could be easily determined via the water contact angles (WCA) measurements. For instance, Dai *et al.* synthesized the E-MA copolymers with good surface properties obtained from α -diimine Pd complexes [161]. The WCA values gradually decreased from 104° to 54° with increasing incorporation of MA monomer. The hydrophilicity of polar-functionalized polymers was reported to strongly related to the structures and contents of the polar groups. Normally, the presence of the hydrogen bond donors in the polar groups (such as -COOH and -OH units) brought about a higher hydrophilicity than the rest of polar monomers [65,78,162]. The stereochemistry of the polar monomers and the microstructures of the copolymers also affected the polymeric surface property (hydrophilicity). In contrast, with the use of α -diimine Pd complexes it was much more challenging to directly achieve the P-TPE materials due to the superior chain-walking tendency [161–163]. It led to the formation of the highly branched (amorphous) polymers with poor mechanical properties. Recently, Dai *et al.* reported the synthesis of polar functionalized P-TPE via the ethylene copolymerization with 10-undecenoic acid catalyzed by the α -diimine Pd complexes [163]. The polar copolymers displayed characteristics of thermoplastic elastomers with

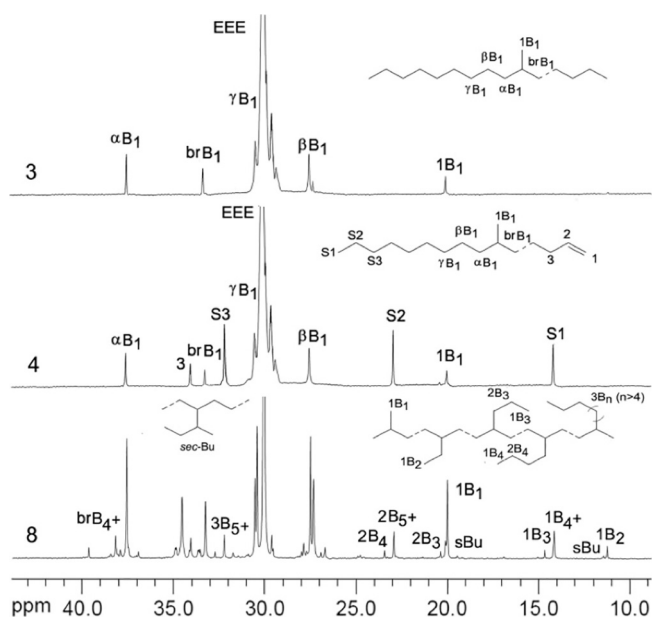


Fig. 43. Reported results on the high temperature ^{13}C NMR spectrum of the branched polymers. Reprinted with permission from Ref.55.

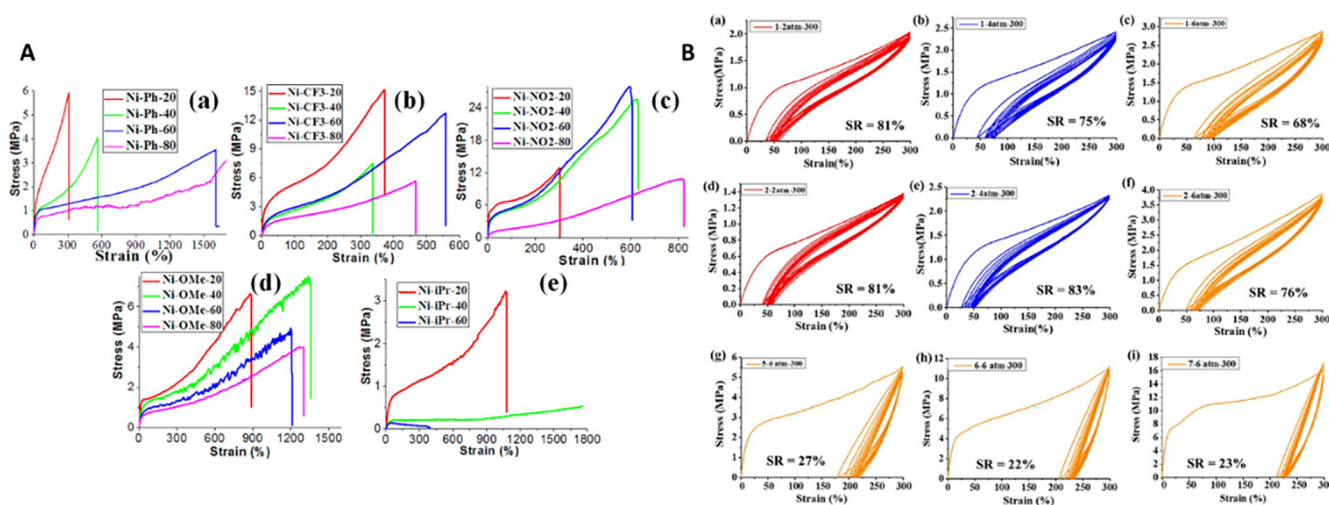


Fig. 44. Reported results on the stress-strain curves (A) and hysteresis loops (B) of the branched polymers. Reprinted with permission from Ref.83 and Ref.164.

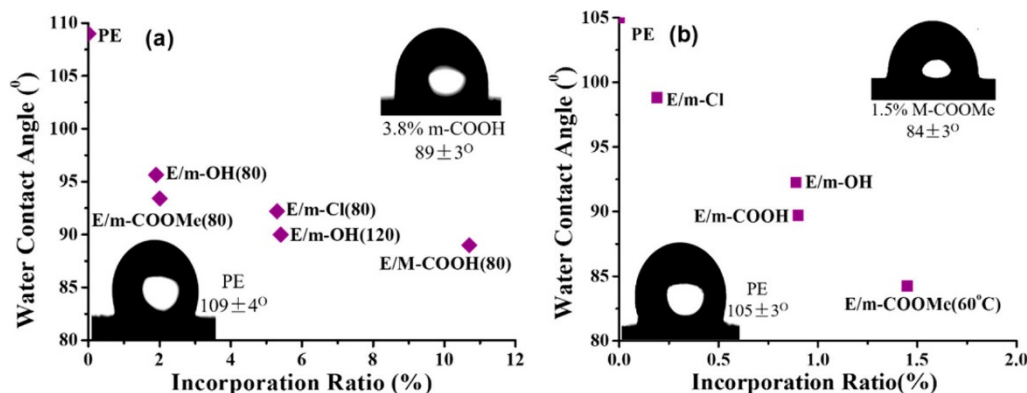


Fig. 45. Reported results on the water contact angles of the polyethylene and copolymers containing polar units. Reprinted with permission from Ref. 80.

great elastic recovery (SR = 72 %–80 %) (Fig. 44B), while the good surface properties enabled by polar monomers was well pronounced at the same time.

6. Conclusion and outlook

This review summarizes the recent advances in the synthesis of the α -diimine Ni and Pd complexes applied in ethylene (co)polymerization. These α -diimine metal complexes achieved very high catalytic activities and thermal stability in ethylene (co)polymerization. The molecular weight, dispersity, branching densities, and melting points could be directly modulated via the finely controlled chain-walking mechanism. The synthesis of high-value polymers such as elastic polymers, LLDPEs, UHMWPEs, and functionalized copolymers can be realized by the ethylene monomer as the main feedstock. Although there are lots of advances in homogenous polymerization, the heterogeneous domains the industrial application. It is clear that the majority of current efforts in the development of α -diimine Ni and Pd complexes are more focused on homogenous (co)polymerization systems. Nevertheless, many fails and errors are inevitable along with the catalysis developments. The reports on heterogeneous polymerization catalyzed by these complexes are still rare. As the homogenous platform is well studied and established, the successful heterogenization of the well-defined α -diimine Ni and Pd complexes could become the primary research emphasis in the future. Due to the unique catalytic performance, these late-transition metal complexes can compete with or outperform present-day catalysts. This heterogeneous strategy will ensure the further control of the polymeric microstructure, morphology, and macro performance on an industrial scale.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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