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Recent Advancements in Nickel-catalyzed Olefin Polymerization: Molecular Design, Mechanistic Insights, and Sustainable Polyolefin Materials

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Abstract Polyolefins, defined as polymers that are widely synthesized, are significant to modern civilization owing to their flexibility and affordability. Nevertheless, conventional polyolefins have limitations in terms of their sustainability and usefulness. Recent innovations in nickel-based catalysts have radically altered olefin polymerization, facilitating precise regulation of the polymer microstructure and integration of polar monomers. This review addresses the recent developments in *α*-diimine nickel catalysts, SHOP-type systems, and iminopyridyl-based complexes, focusing on the impact of steric and electronic ligand alterations on thermal robustness, catalytic activity, and molecular weight control. To clarify its function in adjusting the mechanical and thermal characteristics, the chain-walking mechanism, which is essential for creating branched architectures, was broken down. Breakthroughs, including supramolecular shielding and fluorine effects, in addition to dinuclear architectures, have led to ultrahigh-molecular-weight polyethylenes (UHMWPEs), semicrystalline materials, and thermoplastic elastomers directly from ethylene. In addition, the resulting approaches for copolymerizing ethylene with polar monomers (acrylates, norbornene) or carbon monoxide have revealed routes to functionalized and photodegradable polyolefins. Despite these outcomes, challenges remain in accomplishing highly polar comonomer incorporation and commercial scalability. This review highlights nickel catalysts as an adaptable framework for sustainable polyolefin innovation, connecting academic research with applications in packaging, biomedicine, and recyclable materials.

Keywords Polyolefins; *α*-Diimine nickel catalysts; SHOP-type systems; Iminopyridyl-based complexes; Ultrahigh-molecular-weight polyethylenes

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1 INTRODUCTION

Polyolefins are the predominant category of synthetic polymers produced and utilized globally owing to their superior characteristics, including exceptional formability, low density, and commendable chemical resistance.[1,2] Currently, more than 300 distinct grades of polyolefins are commercially available. Polyethylenes (PE) and polypropylenes (PP) are primary materials manufactured by the petrochemical sector.[2–4] Collectively, they represent the predominant category of commercial polymeric materials.[5] Owing to significant advancements in catalyzed polymerizations, the yearly output of polyethylenes surpasses 180 million tons, accounting for approximately 50% of worldwide plastic production, and is mostly utilized in applications such as film, piping, sheets, product packaging, electronic gears, and medical consumables. They play a crucial role in social production and existence. Conventional polyolefin materials, primarily nonpolar substances such as polyethylene and polypropylene, exhibit limitations in various domains, including printability, adhesion, barrier characteristics, flexibility, compatibility, rheology, and processability. The introduction of a small quantity of polar functional groups (even 0.5 mol%) can significantly ameliorate these deficiencies, expand the applicability of polyolefin materials, and enhance their commercial value. De-

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spite environmental issues, their superior mechanical performance offers significant advantages over bio-based alternatives.[6–9] Brookhart's *α*-diimine catalysts marked a significant advancement in coordination-insertion olefin polymerization, ushering in a new age when late transition metal catalysts dominated the industrial synthesis of polyethylenes.[10,11] The advancement of high-performance olefin polymerization catalysts has remained a significant driving factor in this domain. Catalysts employed in olefin polymerization generally feature electrophilic, high-valent, unsaturated metal centers that coordinate with a monomer, leading to their insertion into the metal-alkyl bond. Since then, significant efforts have been dedicated to the advancement of this catalyst system, with the objective of enhancing catalytic parameters such as activity, polymer molecular weight, and branching density.[12–17] Ultrahigh molecular weights (10^6–10^7 g·mol^{-1}) are highly desirable for polyethylenes (specifically ultra high molecular weight polyethylenes (UHMWPEs)) because of their biological stability, chemical stability, high impact toughness, and exceptional abrasion resistance, making·molecular weight a critical parameter for polyolefins. Multiple techniques have been applied to benchmark *α*-diimine systems to access UHMWPEs. The primary benefit of coordination-insertion chemistry is its exceptional control over the polymeric microstructure, which also dictates the macromolecular properties of polymers, including their mechanical, thermal, and optical characteristics and, consequently, their ultimate commercial values.[17–21] Consequently, an increase in the catalytic performance of organometallic catalysts in ethylene (co)polymerization is a fundamental driving force in catalyst research (Fig. 1).

Since the pivotal scientific breakthrough of coordination olefin polymerization by Ziegler *et al.*[22] and Natta *et al.*[23] in the 1950s, olefin coordination polymerization has attracted significant interest from both academic and industrial sectors, especially those involving early transition metal catalysts, and late transition metal catalysts have achieved excellent activity for ethylene polymerization, yielding a diverse range of branched polyolefins (Fig. 2a).[1] Based on the catalyst structures and polymerization conditions (temperature as well as ethylene pressure), due to the capability of the propagating metal-alkyl species to relocate along the expanding polymer chain such as through rapid-hydride elimination and reinsertion (chain-walking). In contrast to the immensely active early transition-metal catalysts, adaptable late transition-metal catalysts invariably endure poor thermal stability and substantial chain transfer reactions; hence, ligand frameworks with diverse electronics and sterics in these catalysts are pivotal for boosting olefin (co)polymerization. There is a tremendous desire to boost the catalytic activity, enhance the polymer structure and comonomer content, and minimize the cost of the polymerization process. A full understanding of the catalyst structure-property relationship of the catalyst, as well as its exact involvement in the polymerization process, has permitted the synthesis of polyolefins with finely regulated microstructures and varied physical qualities. Olefin polymerization catalyzed by late transition metal complexes has attracted tremendous attention over the past decade, notably after Brookhart's study of Palladium(II) and nickel(II) diimine catalyst systems, which exhibited remarkable catalytic activity for both ethylene and *α*-olefin polymerization.[1–3,24–26]

In general, Ziegler-Natta-type early transition metal catalysts are poisoned by functional groups owing to their high

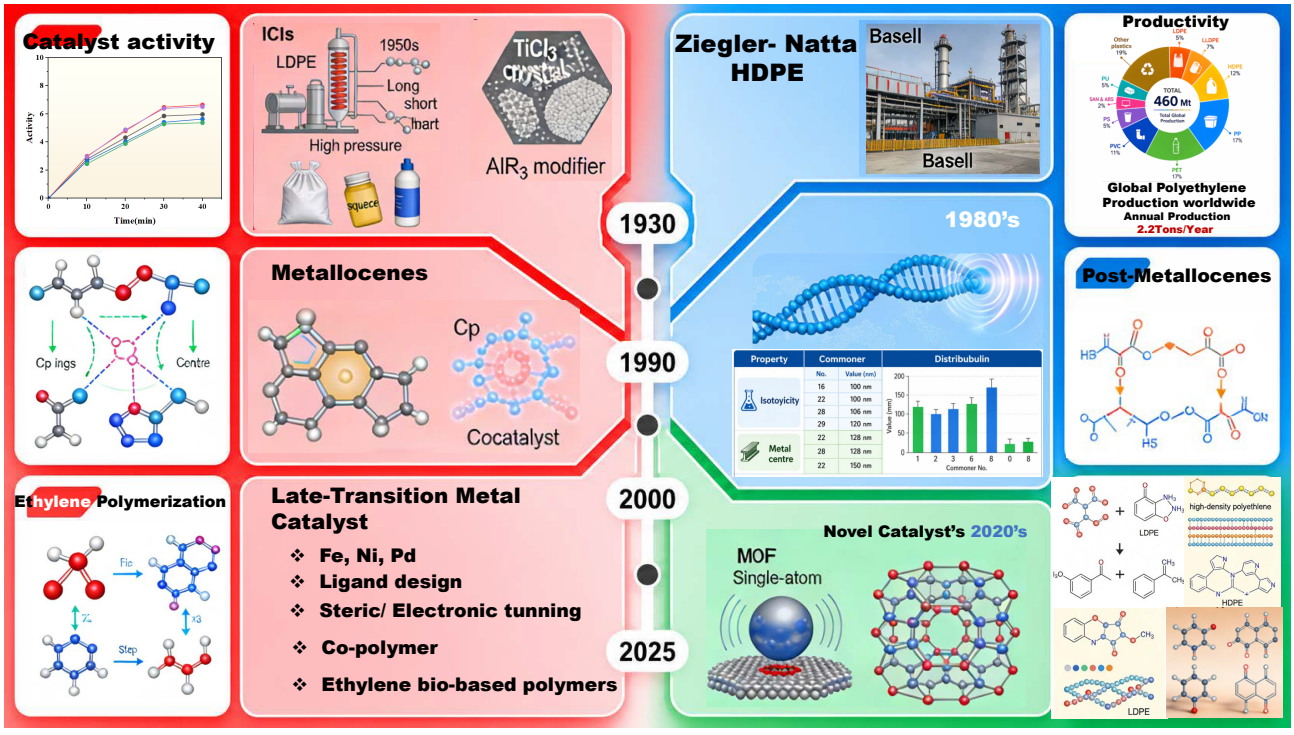

Fig. 1 Development of catalysts in ethylene polymerization.

oxophilicity. It can be challenging to use these catalysts for copolymerizing olefins with polar monomers, particularly those with functional groups directly linked to double bonds (fundamental polar monomers). Compared to their early transition metal counterparts, late-transition metal organometallics have attracted considerable attention owing to their low oxophilicity and potential to produce polymers with polar functional groups and various types of branches.[12,27–39] The utilization of different metal complexes can lead to different catalytic and polymeric properties. Several investigations have been conducted on ethylene polymerization employing N-N bidentate pre-catalysts ligated by *α*-diimine,[40–43] iminopyrrolyl,[44] iminopyridyl,[45] and other ligands. Consequently, the design and production of new nickel and palladium catalysts have long been at the forefront of polyolefin research. It was previously assumed that late transition metal catalysts create oligomers owing to rapid-hydride elimination.

In the 1980s and the 1990s, researchers successively developed metallocene and pre-transition metal catalysts.[46,47] After several years of improvement, these systems have greatly improved their performance, possessing high activity, heterogeneous catalysis, stereoselectivity, and other properties.[48–58] However, this study has many limitations. Pre-transition metals (such as titanium, zirconium, and hafnium, *etc.*) have strong Lewis acidity, whereas polar functional groups are Lewis basic, which easily chelate with metal centers, making it difficult for ethylene monomers to coordinate and insert, thereby leading to catalyst deactivation. Compared to front transition metals, rear transition metals have lower electronegativity, reduced inhibition of heteroatoms, and are less susceptible to poisoning by polar functional groups, making them more promising for the synthesis of polar polyolefin materials. Among late transition metal catalysts, nickel-based catalysts with low cost, low toxicity, and high catalytic activity are favored by the industry. In recent years, researchers have reported nickel-based catalysts with various ligand structures (such as *α*-diimide, salicylaldehyde imine, phosphonic acid, phosphophenol, diphosphine oxide, and *N*-heterocyclic carbene), as well as new strategies for catalyst design (such as steric hindrance and electronic effect regulation strategies, secondary metal cation strategies, external stimulus response regulation strategies, and catalyst heterogeneity strategies).

Catalysis is fundamental to contemporary chemical innovation and connects academic research to industrial applications. The shell higher olefin process (SHOP) represents a significant advancement in homogeneous catalysis, utilizing chelated Ni(II) complexes to selectively oligomerize ethylene into linear *α*-olefins (LAOs), which are essential feedstocks for surfactant, lubricant, and polyethylene production. Since the launch of commercialization in the 1970s, SHOP has transformed the chemical industry and established a fundamental framework for analyzing the relationship among transition metal coordination geometry, electronic modification, and catalytic selectivity. The importance of SHOP catalysts has transcended their industrial application. The 1995 discovery by Brookhart *et al.* of cationic Ni(II)-diimine complexes that can generate high-molecular-weight polyethylene (PE) represents a significant advancement, questioning previously established beliefs regarding the constraints of late transition metals in polymerization catalysis. This groundbreaking discovery redefined olefin polymerization by revealing that nickel, previously dismissed for its chain-transfer-prone reactivity, can achieve controlled polymer growth. This study highlighted the unexplored capabilities of late transition metal catalysts, especially their distinct mechanistic pathways, including chain-walking, and their ability to tolerate polar functional groups. Currently, SHOP-inspired catalysts represent a significant intersection between industrial importance and scholarly interest. Recent developments in ligand design, mechanistic spectroscopy, and computational modeling have enhanced our understanding of nickel redox behavior, migratory insertion mechanisms, and the influence of chelate dynamics on the suppression of *β*-hydride elimination.[36] The movement towards sustainable chemistry has revitalized interest in these systems because of their capacity to oligomerize bio-derived olefins and copolymerize ethylene with polar monomers, a domain traditionally led by early transition metals.

Since this groundbreaking discovery, several modified bidentate nitrogen ligands such as bipyridine ligands and iminopyridine molecules have been reported. Branched polymers with chain topology have the potential to enhance polymer melt tensile properties, ductility, paintability, and compatibility with certain other materials when compared to standard linear PEs.[59,60] Owing to their unusual physical features and prospective use as lubricants, adhesives, and paints, interest in highly branched ethylene oligomers has increased in recent years. Iminopyridyl-based nickel and palladium catalysts can polymerize ethylene to yield low-molecular-weight branching oligomers, and their catalytic activity is higher than that of Brookhart-type-diimine catalysts.

As part of this review, we intend to provide and mainly introduce nickel-based catalysts with different ligand structures with a comprehensive overview of this field with respect to mechanistic details, chain walking polymerization and copolymerization reactions, selected catalysts for chain walking polymerization, and the synthesis and applications of new polymer materials. A comprehensive study clarified the impact of the late transition metal ion, iminopyridyl backbone, and ligand, in addition to the impact of the polymerization conditions on the performance of the catalyst, the extent of branching, the molecular weight and distribution of the polymer, and the characteristics of the polymer products. The present overview analyzes the development of SHOP catalysts, tracing their industrial origins and highlighting their emerging functions as adaptable platforms for precision oligomerization and polymerization. This analysis examines significant advancements in catalyst architecture, mechanistic insights, and innovation driven by applications, while also addressing ongoing challenges related to activity, stability, and stereo control. This study contextualizes recent advances in the broader transition to earth-abundant metal catalysis, highlighting potential pathways for next-generation systems that integrate industrial efficiency with molecular-level precision. In addition to discussing catalysts bearing *α*-diimine ligands, we briefly discuss other catalysts used for chain-walk-

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ing polymerization.

2 CHAIN-WALKING MECHANISM IN ETHYLENE POLYMERIZATION

Ethylene polymerization, a prevalent polymer in industrial applications, is an essential step in the synthesis of polyethylene. Polyethylene is produced by the polymerization of ethylene monomers, a process that may be enhanced by different catalysts, such as Ziegler-Natta catalysts, metallocene catalysts, and, more recently, single-site catalysts. A comprehensive understanding of the polymer microstructure can elucidate monomer enhancement, encompassing insertion selectivity and chain walking paths. The use of *α*-olefin monomers that yield branching polymers *via* early transition-metal catalysts to Ni(II) and Pd(II) *α*-diimine catalysts introduces complexity. Important features, including crystallinity, chain branching, and molecular weight distribution, are affected by this process, which is crucial for determining the microstructure of the resulting polymer. Chain propagation, chain transfer, chain isomerization, and chain walking are the three stages that follow the catalyst initiation mechanism. The catalysts for ethylene oligomerization and polymerization often share the first two stages. Despite the rarity of early transition metal catalysts, the chain-walking mechanism plays a significant role in the olefin polymerization and copolymerization processes catalyzed by *α*-diimine Pd(II) and Ni(II). Chain walking is a defining characteristic of these catalysts. Chain propagation transpires when many cycles of the coordination–insertion mechanism result in elongation of the alkyl chain. One key advantage of this coordination–insertion process compared to other polymerization methods is that its characteristics are predominantly determined by the catalyst structure. Consequently, it is feasible to regulate the molecular weight (by chain transfer), microstructure, and even stereochemistry of polyolefin products derived from coordination–insertion mechanisms. Historically, the predominant method for developing novel olefin polymerization catalysts has relied on trial and error, followed by the refinement of potential lead compounds through the adjustment of their electronic and steric traits. Fink and co-workers[61,62] were the first to characterize the chain-walking mechanism of ethylene polymerization, which was subsequently further developed by Brookhart and co-workers.[63–65] Brookhart *et al.* initially investigated *α*-olefin polymerization using a nickel *α*-diimine catalyst and discovered that poly(*α*-olefin)s generated by chain-walking catalysts exhibit unique microstructures, resulting in physical properties that differ from those of poly(*α*-olefin)s synthesized by early transition metal catalysts.[66] A structural feature is that poly(*α*-olefin)s produced by chain-walking polymerization have much fewer branches than those synthesized using early transition metal systems. During polymerization, the primary alkyl-agnostic complex may undergo *β*-hydride elimination and subsequent reinsertion into the olefin hydride intermediate, resulting in either the original primary alkyl-agnostic complex or a novel secondary alkyl-agnostic complex with reversed regiochemistry. This signifies the initial phase of the chain walking procedure. The trapping of ethylene by the secondary alkyl species, followed by further insertion, led to the creation of a methyl branch in the polymer backbone. Subsequent chain walking over the polymer results in the formation of elongated branches. This step may be repeated many times until the agnostic complex can be captured by the olefin to continue chain propagation, as depicted in Fig. 2(b). The rate of chain walking was approximately 100 times greater than that of monomer insertion with the *α*-diimine Pd(II) catalyst at ambient temperature.[67]

3 *α*-DIIMINE NICKEL CATALYST

In 1995, Brookhart's initial report on *α*-diimide nickel and palladium catalysts was a pivotal discovery in olefin polymerization (Fig. 2a), signifying substantial advancement in the copolymerization of ethylene and polar monomers. The chain-walking process (Fig. 2b) is a notable characteristic of *α*-diimide catalysts[67,68], denoting the fast relocation of metal centers along the polymer backbone *via* *β*-H elimination and reverse insertion of double bonds. Traversing to a certain location initiates ethylene coordination insertion, potentially resulting in varied branching and formation of distinct topological structures. As a result of the aforementioned polymerization mechanism, polyethylene synthesized with an *α*-diimide palladium catalyst frequently exhibits a significant degree of branching (90/1000C) and is typically an amorphous, viscous substance lacking a melting point, characterized by suboptimal processing properties and negligible industrial use. In the catalytic process of ethylene polymerization using an *α*-diimide nickel catalyst, a competitive interaction exists between the chain-walking mechanism and the coordination insertion of ethylene. The degree of branching of the polymer is primarily dependent on the pressure of ethylene. Moreover, increasing the polymerization temperature enhances the chain-walking rate.

In terms of polymerization activity, the *α*-diimide nickel catalyst has the characteristic of high catalytic activity, which is due to the aluminum cocatalyst removing the coordinated halogen atoms, forming highly electron-deficient cationic active centers, and promoting the coordination insertion of ethylene molecules. The molecular weight of polymers is greatly influenced by the electronic and steric hindrance effects of the catalyst skeleton. Specifically, when the aryl group contains a large steric hindrance substituent at the adjacent position, the *β*-H elimination reaction is inhibited, which slows down the chain transfer reaction, accelerates the chain growth reaction, and leads to an increase in the molecular weight of the polymer. When the aryl group is a strong electron-donating substituent (such as —OMe), the lifespan of the catalyst is extended at high temperatures and tends to yield high-molecular-weight polymers. When the aryl group is substituted with an electron-deficient substituent (such as $-CF_3$), the catalyst is more prone to deactivation and the formation of oligomers.

Compared to palladium catalysts, nickel has a higher electronegativity; therefore, *α*-diimide nickel catalysts can be poisoned and deactivated by polar monomers (such as methyl acrylate). Furthermore, polar functional groups can only be copolymerized with methylene groups attached to double bonds (such as long-chain esters).[13,15] Recently, researchers have explored methods to improve olefin polymerization performance by altering the chemical environment of the metal centers, modifying the spatial configuration of ligands, and employing dual-core catalysts.[28,32,69–84]

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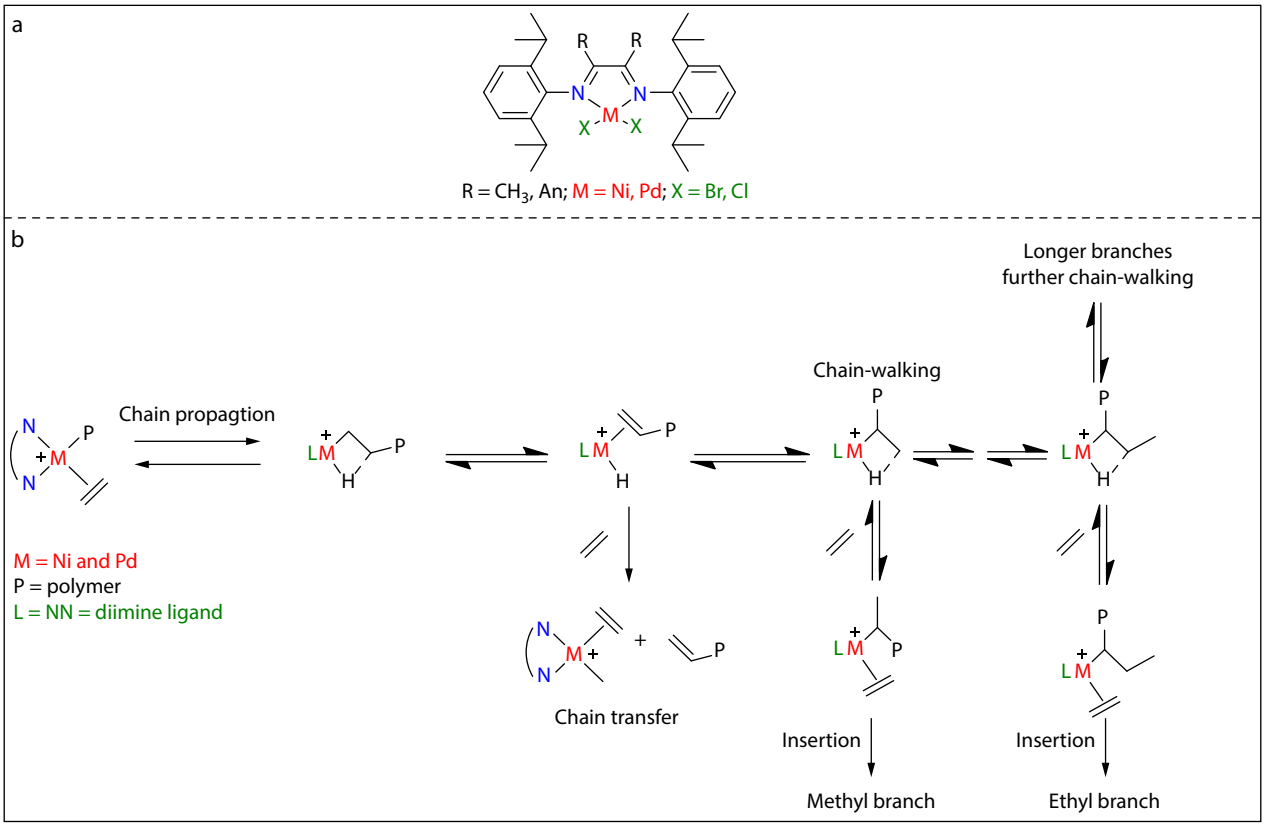

Fig. 2 (a) Structure of *α*-diimine catalysts;[68] (b) General mechanistic of chain walking[67].

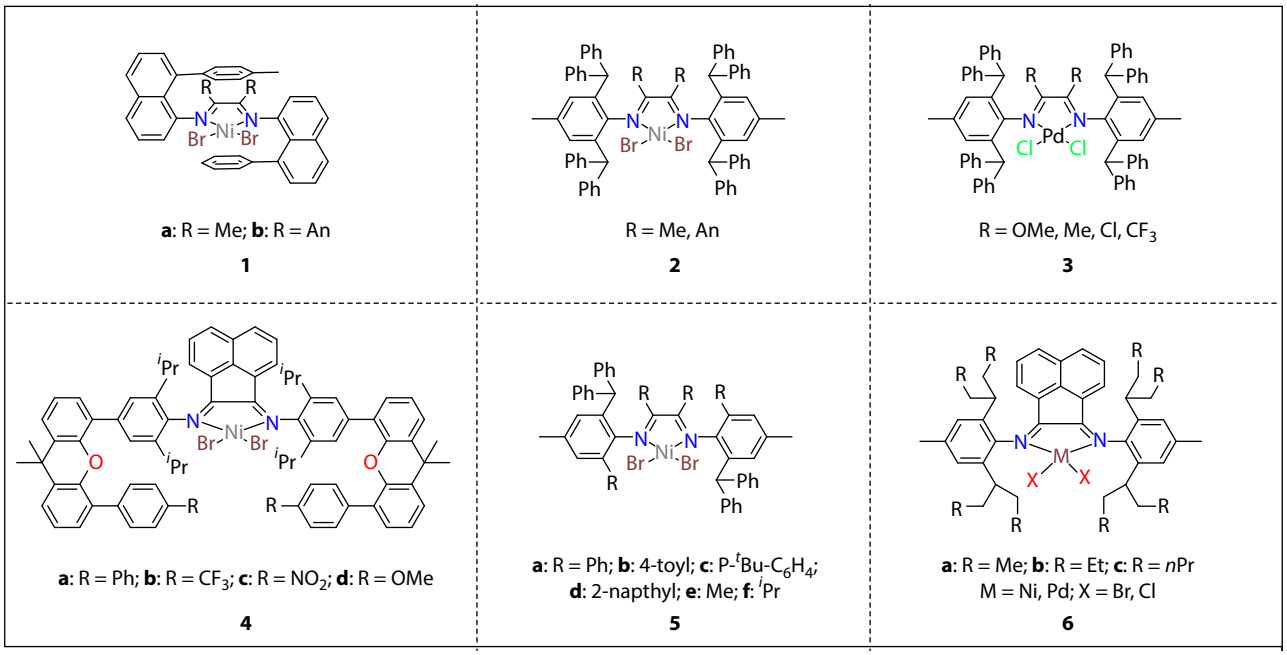

Fig. 3 Selected examples of *α*-diimine Ni(II) complexes.[85–90]

In 2013, Brookhart[85] successfully synthesized a sandwich-structured *α*-diimide nickel catalyst (Fig. 3, catalyst **1**). As a result of the sandwich structure, axial hindrance is improved, and a shielding effect is created on the metal center, reducing chain transfer reactions between the metal center and the monomer. Therefore, catalyst **1** can facilitate the production of high molecular weight polyethylene (M_n can reach up to 178.1×10^4 g·mol^{-1}). It is noteworthy that catalyst **1** is capable of preparing highly branched polyethylene (branching degree 69/1000C–93/1000C) at room temperature, thus laying the foundation for the synthesis of polyolefin materials with high processing readiness.

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In the same year, Long and co-workers[87] designed and synthesized a highly hindered *α*-diimide nickel catalyst with diphenylmethyl substitution (Fig. 3, catalyst **2**). The catalyst's primary attribute is its excellent thermal stability, enabling it to catalyze ethylene polymerization with significant activity (up to 2.8×10^6 g·mol$_{Ni}^{-1}$·h^{-1}) at 100 °C, resulting in high molecular weight polyethylene (23.5×10^4–56.4×10^4 g·mol^{-1}) and a low polydispersity index (1.19–1.46). This study is of substantial importance for the industrial production of ethylene gas-phase polymerization. The features of live polymerization were demonstrated by utilizing this type of catalyst, even at 75 °C. Sterically bulky substituents in *α*-diimine systems enhance the catalyst stability and increase the polymer molecular weight. The outstanding results achieved with catalyst **2** surpassed all expectations and prompted many research groups to delve deeper into the study of related ligands and catalysts.

In 2015, Chen and co-workers[88] developed an improved procedure that can synthesize this type of ligand in yields exceeding 90%. Employing this altered approach, several ligands containing either electron-donating or electron-withdrawing groups (OMe, Me, Cl, and CF_3) were synthesized. In ethylene polymerization, the *α*-diimine palladium catalyst **3** (Fig. 2) demonstrated great thermal stability, activities of up to 3.2×10^6 g$_{PE}$·mol$_{Pd}^{-1}$·h^{-1} (60 °C, 15 min), and high polymer M_n (up to 5.38×10^5). Additionally, it is noteworthy semicrystalline low-density branched (23/1000C–29/1000C) PEs with high T_m of up to 99 °C were obtained. Semicrystalline ethylene/methyl acrylate copolymers can also be prepared through co-polymerizations. This constitutes a remarkable trait for these and subsequently developed diarylhydryl-based *α*-diimine palladium pre-catalysts. A significant number of previously revealed *α*-diimine-based palladium pre-catalysts have led to the development of highly branched (typically >80/1000C) polyethylenes or copolymers. Therefore, completely amorphous polymeric materials with very weak mechanical characteristics have been developed. The ability to restrict the chain-walking process and produce semicrystalline polar-functionalized polyolefins is particularly exciting.

Thermoplastic elastomers (TPEs) have attracted significant interest owing to their recyclability and reprocessing features. This type of material typically comprises a block copolymer, which consists of soft segments that offer viscosity and hard segments that contribute to rigidity. In 2017, Chen and co-workers[86] established a sandwich-like structure for an *α*-diimide nickel catalyst (Fig. 3, catalyst **3**). In contrast with the aforementioned catalysts, catalyst **4** not only has high activity (1.80×10^6–6.94×10^6 g·mol$_{Ni}^{-1}$·h^{-1}), high molecular weight (M_n can reach up to 153.5×10^4 g·mol^{-1}), and high thermal stability, but even more significantly, it is capable of producing polyethylene elastomers. The mechanical properties of these polyethylene elastomers can be altered to a broad range (along with fracture stress values varying between 3 and 28 MPa and fracture strain values ranging from 300% to 1800%). Furthermore, the strain recovery (SR) of the polyethylene elastomer generated by catalyst **4a** with phenyl substitution was over 80%. This study highlights the possibility of synthesizing thermoplastic elastomers utilizing only ethylene as a raw ingredient in a one-pot process.

In 2018, Chen and co-workers[89] synthesized a series of asymmetric *α*-diimine nickel complexes (Fig. 3, catalyst **5**) that showed remarkable properties for ethylene polymerization, producing PE with M_n up to 1.8×10^6 g·mol^{-1}. As a relatively rare scenario for nickel catalysis, this scheme revealed the capability of copolymerizing propylene with polar monomers, such as methyl 10-undecenoate and 10-undecen-1-ol. These complexes were also active in the polymerization of *α*-olefins, including propylene, 1-hexene, 1-octene, and 1-decene. Complex **5d** successfully copolymerized propylene with the polar monomers UAME and UO (incorporation ratios of 0.2 mol%–2.6 mol%)[89]. In contrast, excess methylaluminoxane (MAO) is required for the in situ preservation of polar functional groups. Likewise, catalysts **5e** and **5f** with less bulky substituents demonstrated zero activity for the copolymerization of propylene with UAME and showed lower efficiency for UO/propylene copolymerization.

In 2019, Dai *et al.*[90] successfully synthesized a series of acenaphthene-based *α*-diimine nickel and palladium complexes with systematically varied steric effects, which greatly influenced the catalytic and mechanical properties of the generated PE (Fig. 3, catalyst **6**). These complexes showed high activity (up to 2.1×10^6 g·mol^{-1}·h^{-1}), and branching densities and melting temperatures could be effectively turned over a wide range with M_n (up to 1.2×10^6 g·mol^{-1}). Furthermore, it was intriguing to discover that the branching density of the produced polymers initially increased and then decreased as steric hindrance increased. In contrast, polymer branching for palladium catalysts with comparable ligands continued to decrease as steric hindrance increased. In addition, when activated by Et_2AlCl, these nickel complexes were capable of copolymerizing ethylene with UAME, and the polar comonomer incorporation ratio could be regulated across a wide range (0.17%–2.12%), resulting in functionalized polyolefins with a high molecular weight (up to 242 kg·mol^{-1}).[90] The combined results demonstrate the effectiveness of the catalyst design strategy,compiled in Table 1 and the overall mechanism is illustrated in Fig. 4.

Recently, Jian achieved notable advances in the field of olefin polymerization catalysts.[91,92,95–97] During 2021, Jian and co-workers[91] synthesized *α*-diimide nickel catalyst **7** with various benzene ring configurations (Fig. 5). At standard temperature and pressure, catalyst **7d** may facilitate the polymerization of ethylene to produce ultra-high molecular weight polyethylene (UHMWPE, M_n of up to 6.04×10^6 g·mol^{-1}). Furthermore, catalyst **7d** can facilitate the copolymerization of ethylene with prevalent polar monomers (including esters, carboxylic acids, alcohols, *etc.*) to produce polar UHMWPE, achieving a molecular weight of up to 1.10×10^6 g·mol^{-1}; however, the incorporation of polar units remains comparatively low (0.06 mol%–0.44 mol%). Density functional theory (DFT) simulations suggest that the elevated catalytic activity and synthesis of UHMWPE mostly result from the minimal energy barrier required for the ethylene insertion process.

In 2022, Jian[92] designed a series of *α*-diimide nickel catalysts using a combination of the adjacent fluorine effect and spatial shielding effect to suppress chain transfer reactions. The catalysts **8c–8e** (Fig. 6) containing adjacent fluorine

Table 1 *α*-Olefin polymerizations by various late transition metal catalysts. [a]

Entry	Cat.	*T* (°C)	Yield [b] (g)	Act. [b]	M_n [c]	PDI [c]	B [d]	Ref.
1	**1**	25	2.80	1.10	178.1	1.80	71	[85]
2	**2**	100	1.13	–	56.4	1.90	89	[87]
3	**3**	40	3.58	28.6	53.8	1.14	25	[88]
4	**4**	20	3.03	2.53	153.5	1.94	41	[86]
5	**5**	50	0.90	1.8	180.0	1.50	52	[89]
6	**6**	20	2.14	2.14	53.66	1.46	84	[90]
7	**7**	60	3.41	3.41	60.40	1.38	87	[91]
8	**8**	200	0.21	0.04	6.60	1.53	18.8	[92]
9	**9**	120	0.081	0.08	28.0	1.98	38	[93]
10	**10**	90	1.92	2.88	78.9	1.52	24	[94]
11	**11**	30	2.80	1.10	50.4	2.10	82	[38]

Polymerization conditions: [a] toluene as the solvent and $AlEt_2Cl$ as the cocatalyst. [b] The yields and activities are averages of at least two runs. The activity was in units of 10^6 g·mol^{-1}·h^{-1}. [c] M_n is 10^4 g·mol^{-1} and was determined by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C with polystyrene standards. [d] Branching numbers per 1000C were determined by ^{1}H-NMR spectroscopy.

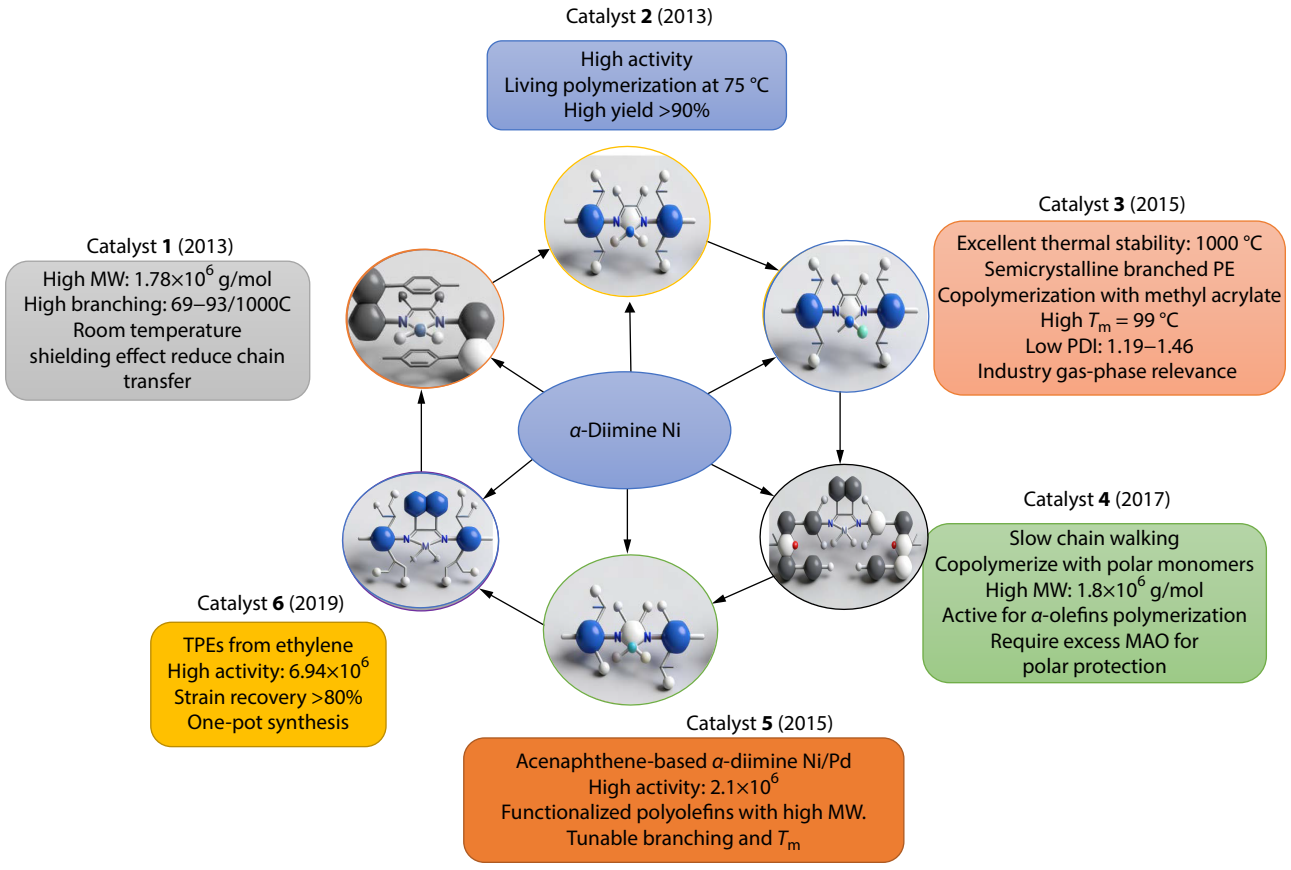

Fig. 4 Structural progression of *α*-diimine Ni(II) catalyst design. The flowchart illustrates key ligand modifications including backbone variation, axial shielding strategies, and substituent electronic tuning and their corresponding impact on ethylene polymerization behavior, molecular weight control, and polyethylene branching architecture.

atoms can catalyze the polymerization of ethylene to prepare semi crystalline low branched polyethylene at a high temperature of 150 °C, but the Polydispersity Index (PDI) is relatively high (1.21–1.25). The research group also synthesized a catalyst **8f** containing a large steric hindrance anthracene group substitution, which further reduced PDI to 1.09 at 150 °C, which is a characteristic of active polymerization. The authors also systematically studied the active polymerization characteristics of catalyst **8f** at 130 °C. Prior to this, there were literature reports that the highest critical temperature for active and inactive polymerizations of ethylene was 90 °C. In addition, catalyst **8c** catalyzed ethylene polymerization under high temperature conditions of 200 °C, and the number average molecular weight M_n of the prepared polymer was 6.6×10^4 g·mol^{-1}. DFT calculations indicate that the above results are due to the high energy barrier that needs to be overcome in chain transfer reactions, which is caused by the synergistic effect of the neighboring fluorine effect and spatial shielding effect, with the neighboring fluorine effect being the main reason.

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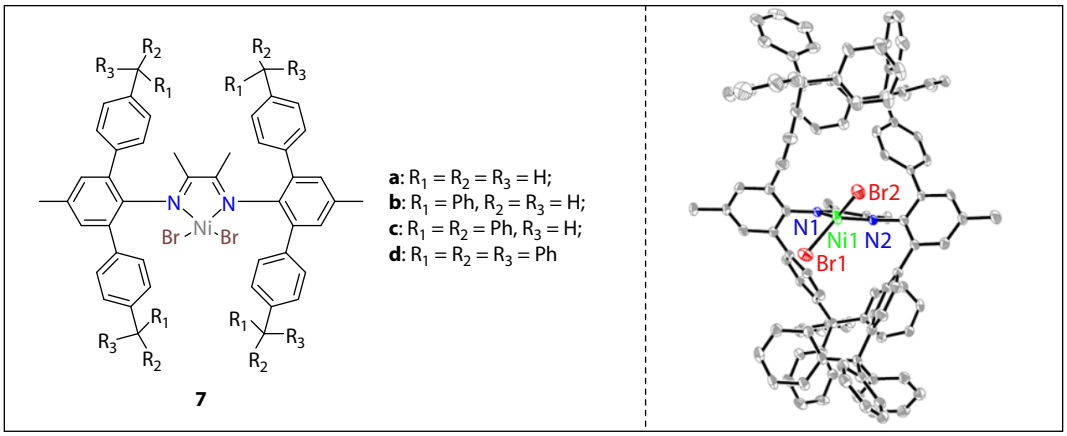

Fig. 5 Well-designed *α*-diimine Ni(II) catalysts prepared by Jian *et al*.[91]

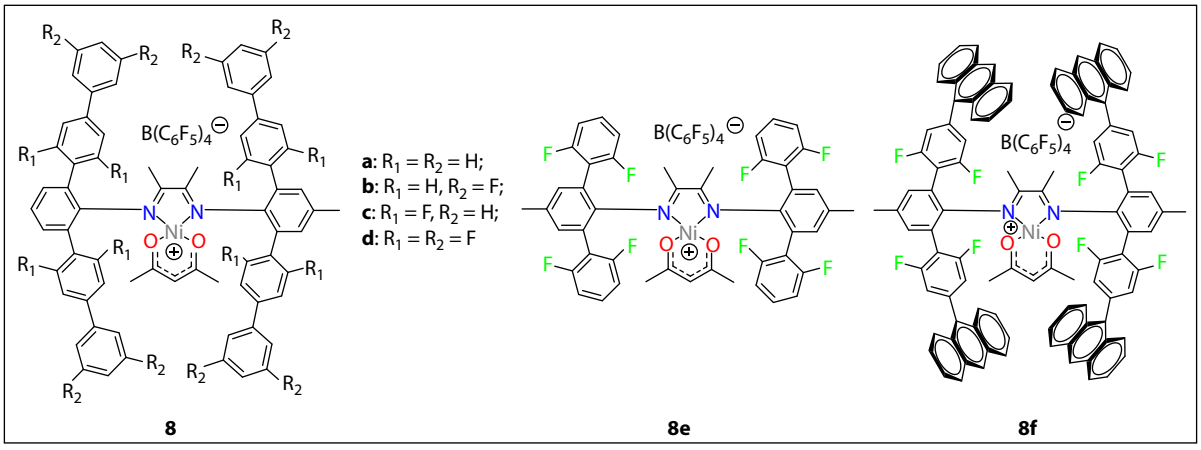

Fig. 6 *α*-Diimine Ni(II) complexes bearing steric shielding and fluorine effects.[92]

The *α*-diimide nickel complex has a typical four coordinated 14 electron structure, and its molecular structure typically presents a high-spin twisted tetrahedral configuration. In 2022, Gao and co-workers[93] designed a planar quadrilateral configuration for an *α*-diimide nickel catalyst (Fig. 7). The author combined a rigid skeleton with a "sandwich" structure to design *α*-diimide nickel catalysts with three-dimensional spatial configurations, namely catalyst **9a** with a dibenzo barrel skeleton and catalyst **6b** with a di naphtho barrel skeleton. Catalyst **9b** still exhibited significant catalytic activity at a high temperature of 120 °C (10^5 g·mol$_{Ni}^{-1}$·h^{-1}). This work presents the first planar configuration of an *α*-diimide nickel catalyst, and the embedding volume ratio of catalyst **9b** was as high as 64.6%, which is the largest spatial hindrance of the reported *α*-diimide nickel catalyst system at that time. In addition, the interaction between nickel and phenyl groups can also inhibit the chain-walking behavior during ethylene polymerization, ultimately resulting in low-branching polyethylene materials (branching degree of 32/1000C–42/1000C).

In 2022, Dai and co-workers[98] designed and synthesized novel unilateral steric "sandwich/semi-sandwich" *α*-diimine Ni(II) and Pd(II) catalysts for ethylene polymerization (Fig. 7, catalyst **9c**). These Ni(II) catalysts afforded moderate activity and high-molecular-weight highly branched polyethylene, and the hybrid sandwich Ni(II) catalyst produced ultra-highly branched polyethylene (146/1000C–168/1000C) with an anomalous temperature-dependent branching trend, such as decreasing density with increasing temperature. The Pd(II) catalysts also showed moderate activity, generating hyperbranched polyethylene, with the hybrid sandwich Pd(II) catalyst delivering a higher branching density and molecular weight than semi-sandwich analogs, along with optimal E-MA copolymer branching and incorporation. Overall, the hybrid sandwich structure enabled the efficient synthesis of highly branched polyethylenes and copolymers *via* Ni/Pd catalysis.

In the same year, the same group[99] developed novel "sandwich/semi-sandwich" *α*-diimine Ni(II) and Pd(II) catalysts featuring dibenzosuberyl substituents, which effectively suppressed chain transfer and increased the polymer molecular weight (Fig. 7, catalyst **9d**). The Ni(II) catalysts showed high activity (10^6 g·mol^{-1}·h^{-1}) and afforded ultra-highly branched polyethylene with exceptional molecular weights (up to 586.4 kg/mol), alongside an anomalous temperature-dependent branching trend contrary to prior reports. The Pd(II) catalysts exhibited moderate activity (10^5 g·mol^{-1}·h^{-1}), yielding high-molecular-weight branched polyethylene and E-MA copolymers with favorable incorporation ratios, and the dibenzosuberyl catalysts outperformed classical dibenzhydryl analogs, lifting the polymer molecular weights by 1–2 orders of magnitude *via* the unique sandwich-like steric structure.

In 2023, the research group led by Dai and co-workers[94] designed and synthesized two types of *α*-diimide nickel catalysts using dibenzodiene as the skeleton, namely centrally symmetric catalyst **10a** and unilaterally asymmetric catalyst

10b (Fig. 8), with catalysts **10a** and **10b** having almost the same embedding volume. At 90 °C, both catalysts exhibited high activity (above 10^6 g·mol$_{Ni}^{-1}$·h^{-1}) and high molecular weight (M_n>5×10^5 g·mol^{-1}) in catalyzing ethylene polymerization. Surprisingly, catalyst **7a** can obtain semi crystalline polyethylene with high melting point (96–109 °C) and low branching (11/1000C–25/1000C), and catalyst **10b** can prepare highly branched polyethylene without melting point (branching degree of 110/1000C–115/1000C). DFT calculations indicated that catalyst **10a**, with a symmetrical struc-

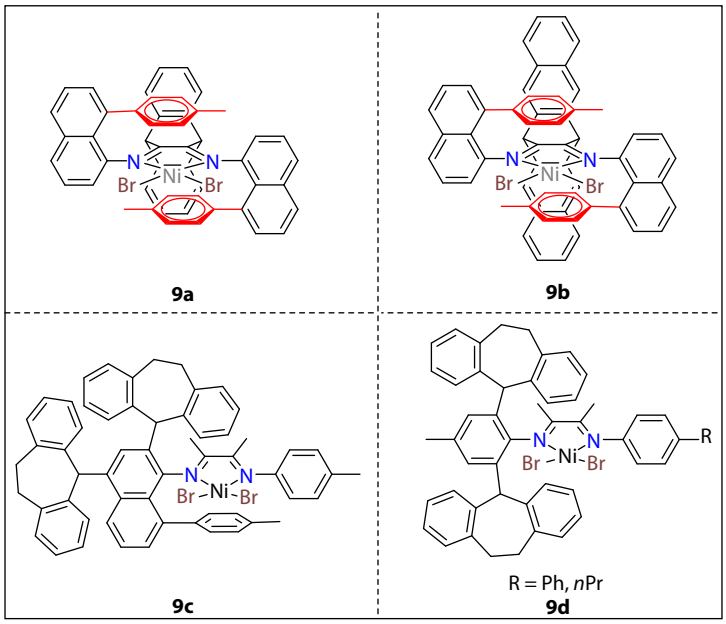

Fig. 7 *α*-Diimine Ni(II) catalysts with bulky backbones.[93,98,99]

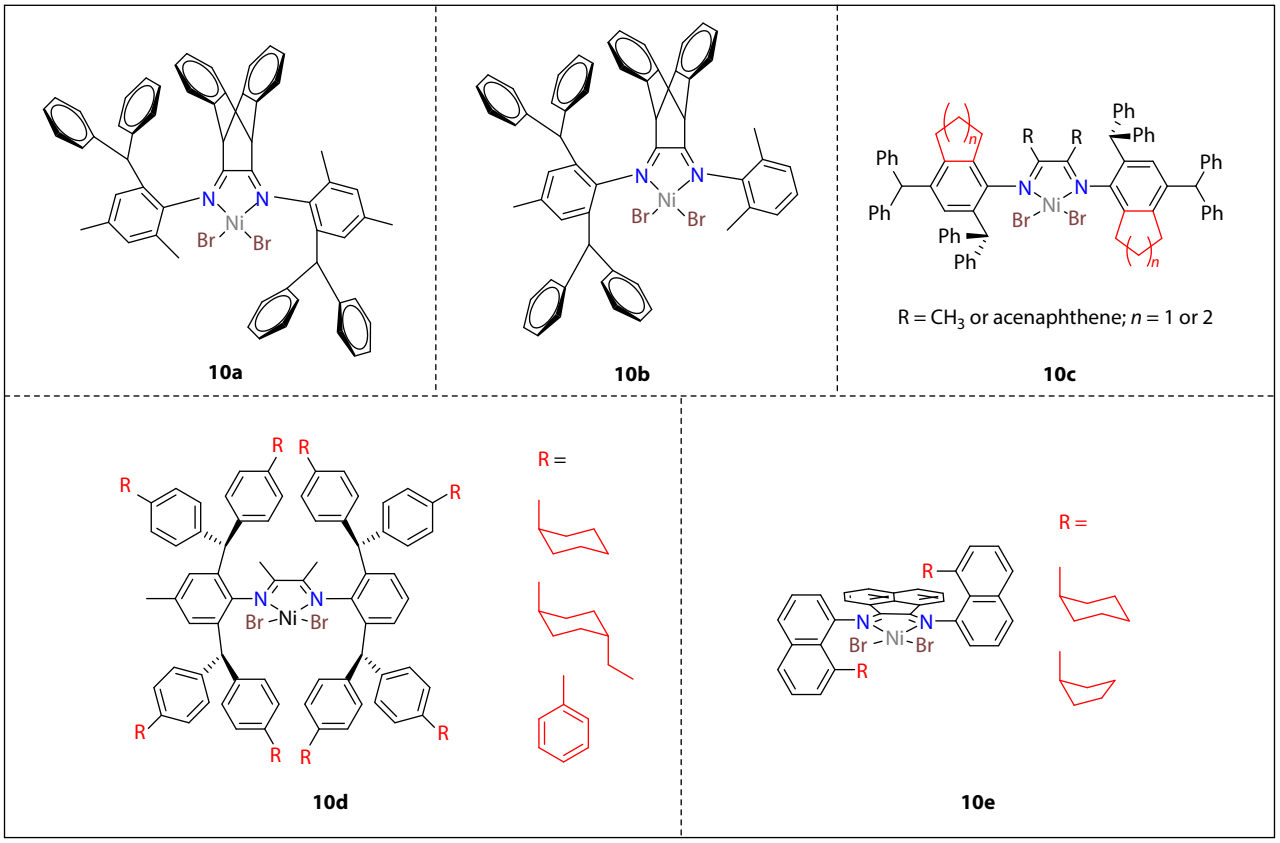

Fig. 8 Tailor-made *α*-diimine Ni(II) complexes synthesized by Dai *et al.*[94,100–102]

https://doi.org/10.1007/s10118-026-3675-9

ture, was more conducive to suppressing the chain-walking behavior.

In 2023, Dai and co-workers[100] developed benzocycloalkyl *α*-diimine Ni(II) complexes (Fig. 8, **10c**) featuring distinct backbone architectures and axial dibenzhydryl groups, which successfully addressed the persistent challenge of producing lightly branched ultrahigh-molecular-weight polyethylene (UHMWPE). In ethylene polymerization, these systems demonstrate exceptional catalytic activities, reaching 10^7 g·mol^{-1}·h^{-1}, yielding polyethylenes with low branching densities (25/1000C–43/1000C) and remarkably high molecular weights (M_n up to 1846 kg·mol^{-1}). Notably, the cationic benzocyclohexyl derivatives enable access to lightly branched UHMWPE (1.05×10^6–1.85×10^6 Da) through enhanced chain propagation rates. The resulting materials exhibited excellent mechanical properties, with high stress and strain at break. In copolymerization studies with methyl 10-undecenoate (MU), these catalysts maintained good productivity while producing copolymers with moderate molecular weights, low branching, and modest incorporation ratios (0.46 mol%–1.63 mol%).

In the same year, the same group[101] synthesized a series of *α*-diimine Ni(II) and Pd(II) complexes featuring a rigid–flexible double-layered steric architecture, incorporating bulky diarylmethyl groups with remote 4-cycloalkyl or phenyl substituents (Fig. 8, catalyst **10d**). In ethylene polymerization, Ni(II) catalysts exhibit high activity (about 10^6 g·mol^{-1}·h^{-1}) and exceptional thermal stability, enabling the production of moderately branched polyethylenes with high molecular weights and narrow dispersities. Notably, these catalysts support living polymerization at elevated temperatures (80 °C), yielding materials with outstanding tensile strength and elastic recovery (strain recovery up to 86%). The Pd(II) analogs displayed moderate activity, producing similar moderately branched, high-molecular-weight polyethylenes with good mechanical properties and moderate elasticity at 60 °C. Furthermore, the Pd complexes facilitated ethylene–polar monomer copolymerization, affording functionalized polyethylenes with moderate branching, molecular weights, and incorporation ratios.

In 2023, Dai and co-workers[102] developed a new class of acenaphthene-based *α*-diimine Ni(II) and Pd(II) complexes incorporating 8-cycloalkylnaphthyl moieties to investigate the effect of flexible axial shielding on ethylene (co)polymerization (Fig. 8, catalyst **10e**). In ethylene polymerization, the Ni complexes demonstrate high activities (up to 1.99×10^6 g·mol^{-1}·h^{-1}), affording slightly branched (34/1000C–54/1000C) polyethylenes with very high molecular weights (M_n up to 1075 kg·mol^{-1}). In contrast, the Pd analogs exhibited moderate activities (about 10^4 g·mol^{-1}·h^{-1}) and yielded highly branched (111/1000C–125/1000C) polyethylenes with moderate molecular weights. In ethylene–methyl acrylate (MA) copolymerization, Pd complexes produce highly branched copolymers (110/1000C–123/1000C) with moderate MA incorporation (1.97 mol%–5.56 mol%).

In 2024, Dai and co-workers[103] concluded a series of studies on *α*-diimine Ni(II) and Pd(II) catalysts, which demonstrated that strategic ligand design, through backbone modification, axial shielding, and electronic tuning, enables precise control over the ethylene (co)polymerization behavior and polymer properties (Fig. 9, catalyst **11a**). Benzocycloalkyl-fused systems with dibenzhydryl groups yielded exceptionally active Ni catalysts (10^7 g·mol^{-1}·h^{-1}) that produced lightly branched ultrahigh-molecular-weight polyethylene (M_n up to 1846 kg·mol^{-1}) with excellent mechanical properties, while rigid–flexible double-layered steric architectures imparted superior thermal stability and enabled living polymerization at 80 °C, affording materials with high elastic recovery (up to 86%). The introduction of flexible 8-cycloalkylnaphthyl shielding revealed that cyclohexyl groups are more effective than cyclopentyl or rigid planar aryl groups in suppressing chain transfer, leading to higher molecular weights and, intriguingly, opposing trends in branching density for Ni (reduced branching) versus Pd (increased branching) catalysts. Furthermore, systematic halogenation (Cl, Br) of o-aryl substituents in dibenzhydryl-based Ni catalysts demonstrates that while steric size governs molecular weight, branching density reflects a balance of steric and electronic effects, and the resulting branched high-molecular-weight polymers function as excellent thermoplastic elastomers (strain at break up to 2478%, strain recovery up to 62%).

In the same year, the same group[104] developed the strategic incorporation of heteroatomic dibenzosuberyl substituents in *α*-diimine Ni(II) and Pd(II) catalysts to effectively modulate chain transfer and chain walking processes through tailored metal–*π* interactions during ethylene (co)polymerization (Fig. 9, catalyst **11b**). In nickel-catalyzed systems, these heteroatomic catalysts exhibit reduced activities and produce polyethylenes with significantly lower branching densities (21/1000C–48/1000C versus 83/1000C–90/1000C) and molecular weights reduced by an order of magnitude (2.3–6.5 kg/mol versus 54.6–89.1 kg/mol) compared to their non-heteroatomic dibenzosuberyl counterparts. Analogous trends were observed in palladium-catalyzed ethylene polymerization and ethylene-MA copolymerization, with sulfur-containing substituents exerting particularly pronounced effects. Mechanistically, weak metal-*π* interactions between the dibenzosuberyl groups and the metal center during catalysis have been proposed to suppress *β*-H elimination while promoting synergistic chain transfer, providing a rational basis for the observed reductions in molecular weight and branching density, and offering valuable insights for the design of catalysts tailored to produce polyolefins with specific microstructures.

Recently, our group[38] synthesized a series of hemilabile *α*-diimine nickel catalysts bearing oxygen atoms as neighboring groups (Fig. 9, catalyst **11c**) to achieve a higher copolymerization activity under elevated temperature conditions. Nickel complexes (Ni1–Ni4) contained adjustable steric hindrance and oxygen atom numbers, influencing the ethylene (co)polymerization processes. Ni2 polymerized with oxygen atoms showed a higher thermal stability than Ni1 without oxygen atoms during ethylene polymerization. These catalysts showed high activity with high molecular weights up to 50.4×10^4 g·mol$_{Ni}^{-1}$·h^{-1}. Moreover, polar monomers were incorporated at higher rates (1.2 mol%) with higher catalytic activity (1.4×10^6 g·mol^{-1}·h^{-1}) during the copolymerization process with ethylene). Meanwhile, owing to the interaction with

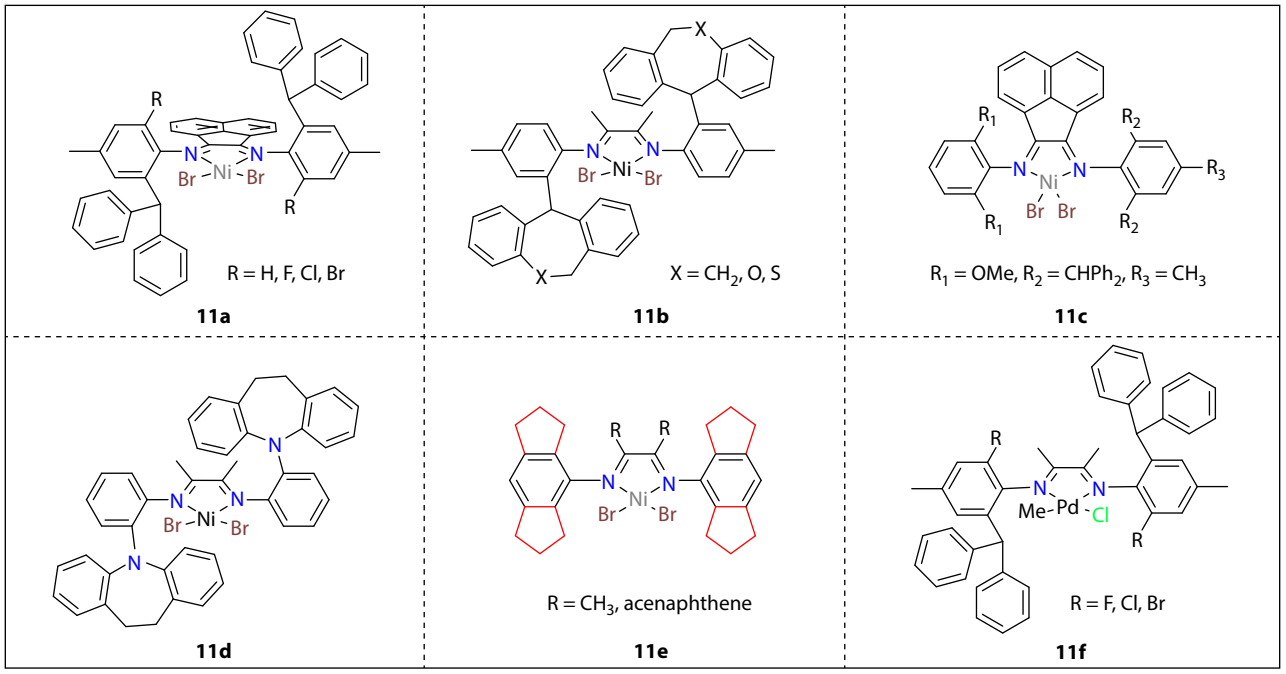

Fig. 9 Hemilabile *α*-diimine Ni(II) complexes.[38,103–107]

the catalytic nickel center, the Ni4 complex with four oxygen atoms was found to be deactivated during ethylene polymerization.

Dai and co-workers[105] in 2024 demonstrated that the incorporation of nitrogen-containing iminodibenzyl substituents into *α*-diimine Ni(II) and Pd(II) catalysts is highly effective in suppressing both chain walking and chain transfer during ethylene (co)polymerization, thereby exerting decisive control over the polymer microstructure and molecular weight (Fig. 9, catalyst **11d**). In nickel-catalyzed ethylene polymerization, the iminodibenzyl-substituted catalyst exhibited significantly higher activity and produced polyethylenes with molecular weights orders of magnitude greater than those obtained using the analogous N-diphenyl catalyst. Comparable trends were observed for palladium-catalyzed ethylene polymerization and ethylene–methyl acrylate copolymerization, where the iminodibenzyl Pd catalyst yielded polymers with substantially higher molecular weights. Notably, relative to their dibenzosuberyl counterparts, iminodibenzyl catalysts demonstrated a superior capacity to curtail chain walking, affording (co)polymers with markedly reduced branching densities.

During the same year, the same group[106] synthesized two bis(benzocyclopentyl) *α*-diimine Ni(II) complexes with varying backbones have been synthesized and evaluated them for ethylene polymerization, revealing a distinctive capability to produce low-molecular-weight polyethylene waxes (Fig. 9, catalyst **11e**). These catalysts exhibit high activities (0.63×10^6–7.23×10^6 g·mol^{-1}·h^{-1}) and yield polyethylene waxes with low molecular weights (2.7–7.8 kg·mol^{-1}) and high branching densities (43/1000C–86/1000C), with the butyl-backbone variant affording significantly higher molecular weights within this range. The axial substituent restriction strategy creates a sterically open structure that reduces molecular weight by over two orders of magnitude compared to unrestricted ethyl analogs, enabling access to wax-grade products with enhanced properties.

Recently, Dai and co-workers[107] systematically investigated o-aryl halogen substitution in dibenzhydryl *α*-diimine Pd(II) catalysts with a butyl backbone and revealed pronounced steric effects on ethylene (co)polymerization behavior, building upon prior observations of nickel analogs (Fig. 9, catalyst **11f**). These palladium catalysts exhibit high activities (10^5 g·mol$_{Pd}^{-1}$·h^{-1}) in ethylene polymerization, producing highly branched (70/1000C–83/1000C) polyethylenes with molecular weights tunable across a wide range (0.9–44.2 kg·mol^{-1}). Critically, the size of the o-aryl halogen governs the molecular weight, with bulkier halogens such as Br and I effecting substantial increases, while their influence on branching density and activity remains subtle, likely reflecting a counterbalance between steric hindrance and electronic effects. In ethylene–methyl acrylate copolymerization, analogous trends emerge: larger halogens hinder MA incorporation, yielding copolymers with lower insertion ratios, yet unexpectedly enhancing the overall copolymerization activity. Representative diimine Ni(II) catalyst architectures discussed in this section, together with their key structural features that govern catalytic activity and polymer microstructure control, are summarized in Fig. 10.

4 SHOP-TYPE NICKEL CATALYST

In the early 1960s, Keim and co-workers[108] introduced a bidentate nickel catalyst with a [P, O] structure, named SHOP the shell higher olefin process (SHOP) catalyst (Fig. 11, catalyst **12**), which has been successfully commercialized for the preparation of ethylene-terminated linear polyethylene oligomers. The framework of the SHOP nickel catalyst itself comprises Ni-C linkages; hence, there is no need to add extra alkylating co-catalytic acti-

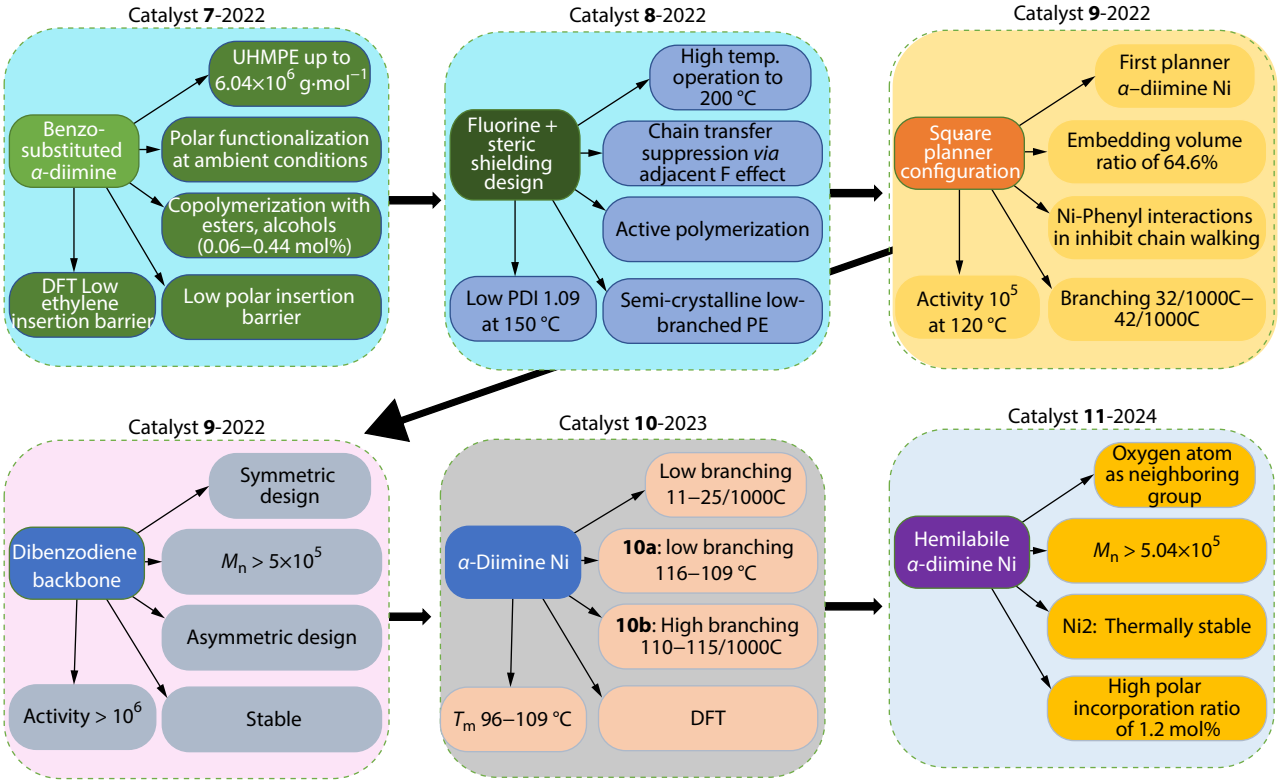

Fig. 10 Summary of recent progress in α-diimine Ni-catalyzed polymerization. Timeline depicting the transition from ambient-condition polar functionalization (2022) to high-temperature thermally stable systems (2024). Key performance indicators such as UHMWPE production, low PDI at elevated temperatures, and tunable branching density are highlighted for each catalyst generation.

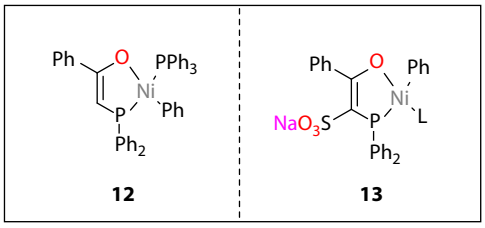

Fig. 11 SHOP Ni(II) catalysts.[108,109]

vation. In the presence of the phosphine scavenger $Ni(COD)_2$, the neutral group PPh_3 exits, resulting in vacancies, allowing room for ethylene coordination insertion. Ethylene coordination inserts Ni-Ph bonds, yielding styrene molecules and generating Ni-H active species; consequently, ethylene constantly enters and the polymer chain increases, and the chain termination process is accomplished by the β-H elimination reaction, accompanied by the regeneration of Ni-H active species and the release of alpha olefin polymer. Consequently, the catalyst commonly catalyzes ethylene polymerization to create oligomers ranging from C8 to C20, with a molecular weight of only a few thousand and a linear shape. The potential of the SHOP nickel catalyst to copolymerize polar monomers is relatively low. In 1989, catalyst **12** (Fig. 11) was originally discovered[109], which contains a sodium sulfonate substituent and can copolymerize polyethylene with some specified polar monomers. The polar functional groups of these monomers are coupled to the vinyl group by at least two methylene units.

E-NB copolymers offer benefits such as a high T_g, high transparency, and high heat resistance, as well as strong physical and mechanical qualities, and have vital applications in many optical lenses. In 2002, Selvy and co-workers[110] (catalyst **13**) revealed that the SHOP nickel catalyst was capable of trigger the copolymerization of ethylene and norbornene (NB) with a molar insertion ratio of NB as high as 50%, yielding a basic alternating copolymer. In response to the significant steric hindrance of Ni NB bonds, it is difficult for the norbornene units to be reinserted, making it difficult to produce continuous norbornene fragments and resulting in reduced norbornene insertion ratios[111,112]. Furthermore, the SHOP nickel catalyst can also copolymerize polar norbornene with oxygen-containing functional groups, although the insertion of polar norbornene is comparatively low, and the polymerization activity and molecular weight are poor.

In 2017, Shimizu and co-workers[113] introduced a class of 2-phosphaphenol nickel catalysts (Fig. 12, catalyst **14**) with alkoxy or phenoxy substituents designed to influence the reactivity of the metal center. Mechanistic studies demonstrated that the oxygen donor atoms participate in restoring stability interactions with the nickel center, which effectively suppresses chain-transfer processes and facilitates the production of high-molecular-weight polyethylene (M_n>10^6 g·mol^{-1}). The implementation of electronic stabilization extends the lifespan of the polymer chain, representing a significant advancement in the production of durable high-performance polyolefins. In addition to ethylene homopolymerization, catalyst **14** exhibited significant adaptability as a single-component framework for the synthesis of ester-functional-

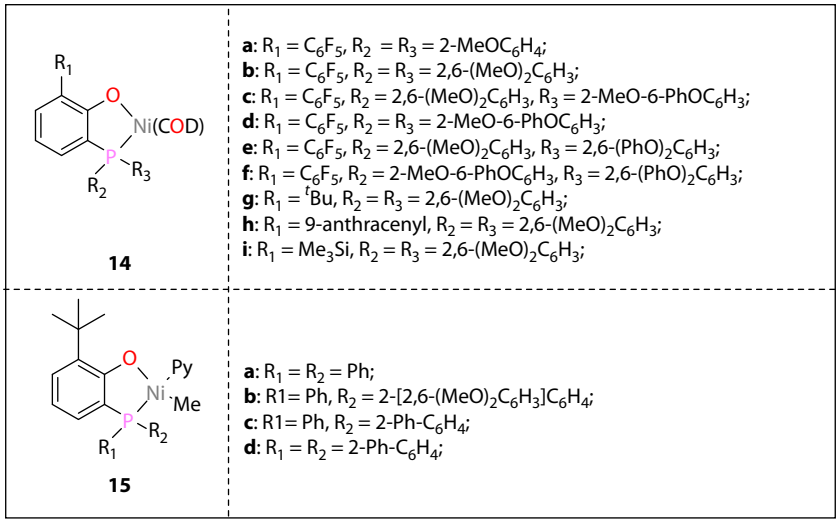

Fig. 12 Phosphine-phenolate Ni(II) catalysts.[113,114]

ized polyolefins *via* copolymerization with polar monomers. The approach demonstrated outstanding control over polar comonomer incorporation, with insertion ratios adjustable from 0.3 mol% to 4.5 mol%, while preserving regioselectivity for positioning functional groups primarily along the polymer backbone. Architectural precision improves the compatibility of polymer blends and adhesives, effectively addressing a persistent challenge in the functionalization of polyolefins. The two-fold purpose of these catalysts, which combines elevated activity for ethylene polymerization with selective polar monomer insertion, demonstrates the complementary significance of ligand design in maintaining electronic and steric effects. The research described here lays the groundwork for next-generation catalysts that may modify the microstructure and function of polyolefins for advanced material applications, including biomedical coatings and recyclable packaging, by utilizing oxygen-mediated metal stabilization.

In 2018, Li *et al.*[114] reported a series of phosphine phenol nickel catalysts containing biphenyl substituents (Fig. 12, catalyst **15**). The authors believe that pyridine is a strong coordinating group; therefore catalyst **24** has good thermodynamic stability (can catalyze ethylene polymerization at 90 °C). Simultaneously, the introduction of biphenyl substituents effectively shields the P orbitals of the nickel centers, increasing the activity of the catalyst and the molecular weight of polyethylene. Catalyst **14** exhibited an activity of up to 10^6 g·mol$_{Ni}^{-1}$·h^{-1} in catalyzing ethylene homopolymerization in the presence of polar solvents (ethanol, ether, acetone, water, acetonitrile, and dimethylformamide) in the polymerization system, with an average molecular weight M_w of up to 7×10^5 g·mol^{-1} for the polymer. In addition, catalyst **14** can also catalyze the copolymerization of ethylene with polar monomers, such as MA, exhibiting moderate activity (1.2×10^3–1.0×10^5 g·mol$_{Ni}^{-1}$·h^{-1}), adjustable monomer insertion ratio (0.5 mol%–13.6 mol%), and low copolymer molecular weight (1.2×10^3–1.08×10^5 g·mol^{-1}).

Phosphophenol-nickel catalysts can also be used to prepare propylene-polar monomer copolymers. In 2018, Nozaki and co-workers[115] reported the first nickel-catalyzed propylene polymerization reaction with a certain regioselectivity and stereoselectivity. They installed a large number of alkyl substituents (tert-butyl and menthol) on phosphine and synthesized a series of nickel catalysts based on phosphophenol ligands (Fig. 13, catalyst **16**). The authors believe that the use of bulky alkyl substituents (such as menthol) on phosphorus atoms is beneficial for the 1,2-insertion of propylene monomers and is crucial for the formation of polypropylene with high stereoregularity ([mm ≤ 68%). In addition, catalyst **16** can catalyze the copolymerization of propylene with polar monomers such as 3-butanol, 3-butene acetate, and *tert*-butyl N-allylamine, with an insertion ratio of polar groups ranging from 0.39 mol% to 2.4 mol%. This study provides a new strategy for the introduction of polar functional groups into hydrophobic polypropylene materials.

In 2019, Dan and co-workers[116] successfully synthesized a series of bulky phosphine-based nickel SHOP-type catalysts (Fig. 14, catalyst **17**) with variable electronic substituents in high yields by employing a facile synthetic route, utilized as single-portion catalysts ahead of ethylene polymerization despite employing any phosphine scavenger. which are challenging to synthesize using previously published synthetic procedures. The aforementioned nickel catalysts demonstrate higher thermal stability with high catalytic activities of up to 10^5 g$_{PE}$·mol$_{Ni}^{-1}$·h^{-1} during ethylene polymerization and well as emerged as highly crystalline linear *α*-olefinic solid polymers with molecular weights of 750–3700 g·mol^{-1}, narrow poly-dispersities (1.48–2.75), and high melting points of

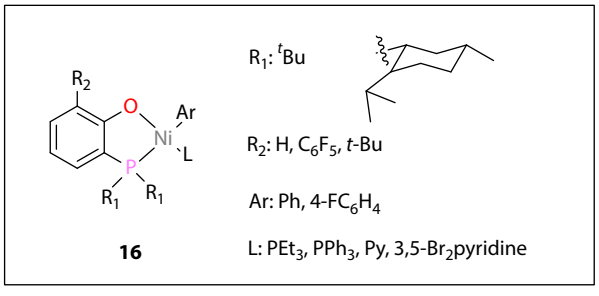

Fig. 13 Nickel complexes bearing bidentate alkylphophine-phenolate ligands.[115]

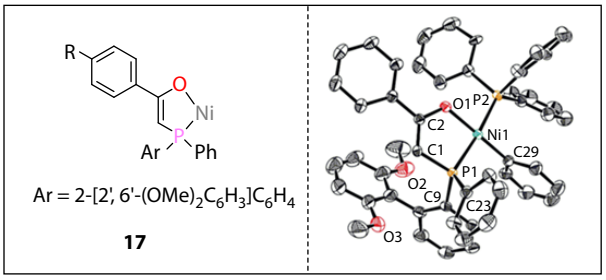

Fig. 14 Shop-type Ni complexes synthesized by Peng Dan.[116]

up to 123 °C. The proposed catalytic achievement of the SHOP-type nickel complexes was notably enhanced by incorporating a bulky ortho-biphenyl group on the phosphorous atom or an electron-withdrawing trifluoromethyl group on the backbone of the ligand, indicating that steric and electronic effects play critical roles in ethylene polymerization catalyzed by SHOP-type nickel complexes.

In the year of 2021, Agapie's *et al*.[117] revealed recently two types of [P,O]-nickel catalysts for the SHOP (Shell Higher Olefin Process) type, demonstrating exceptional catalytic performance in the copolymerization of ethylene and tert-butyl acrylate at 100 °C (Fig. 15, catalyst **18**).The polar monomer incorporation ratio and catalytic thermal stability were both significantly enhanced by the addition of large stiff substituents to the side of the phosphino-phenol ligand. At 100 °C, these catalysts demonstrated high activity (up to 6.4×10^5 g·mol^{-1}·h^{-1}), intermediate molecular weight (M_n up to 23 kg·mol^{-1}), and high polar monomer incorporation ratios (up to 12 mol%). In a recent study, they described a nickel catalyst based on a phosphine-enol ligand for the homogeneous copolymerization of ethylene and tert-butyl acrylate at high temperatures (110 °C). This catalyst produced low molecular weights (M_n up to 13 kg·mol^{-1}), low polar monomer incorporation ratios (up to 1.6 mol%), and high activities (up to 2.4×10^7 g·mol^{-1}·h^{-1}). Catalyst **18a** exhibited excellent performance in catalyzing the copolymerization of ethylene and tert-butyl acrylate, with a high activity (290 kg·mol$_{Ni}^{-1}$·h^{-1}), high molecular weight (M_n >3.1×10^4 g·mol^{-1}), and high insertion ratio (8.70 mol%). Catalyst **18b** has a similar polymerization activity (262 kg·mol$_{Ni}^{-1}$·h^{-1}), but the highest insertion ratio of tert-butyl acrylate was only 1.38 mol%, and the molecular weight was relatively low (M_n >9000 g·mol^{-1}). The author explained that the rigid steric hindrance of oxygen atoms adjacent to the polar monomer tert-butyl acrylate in the structure of catalyst **18a** hinders coordination, while the rotating flexible catalyst **18a** can achieve instantaneous coordination.

Mecking's group[118] acknowledged an accomplishment in 2022: nickel phosphine-phenol complexes (**19a**–**19d**, Fig. 16), which facilitate live microemulsion polymerization of ethylene, building on their groundbreaking work in aqueous polyolefin synthesis. With exact chain-length control, these catalysts produce ultrahigh-molecular-weight polyethylene (M_n up to 2.0×10^6 g·mol^{-1}) with to date remarkable live polymerization properties. It is noteworthy that the systems maintained strong activity at high temperatures (between 50 and 70 °C), surpassing the conventional constraints of thermal instability in the polymerization of live olefins. A distinguishing characteristic of the research being conducted is the single-chain-per-catalyst mechanism: each nickel center originates and propagates a solitary polyethylene chain, which self-assembles into monodisperse nanoparticles (about 50–200 nm in diameter) with a regulated size and shape. This activity emulates biological templating processes, with the catalyst functioning as a nanoreactor that restricts chain development within the surfactant-stabilized micelles.[121,122] The resultant polyethylene nanoparticles demonstrate remarkable crystallinity and thermal durability (T_m>130 °C), attributes essential for high-performance coatings or nanocomposites. The present study realizes three significant advancements by integrating live polymerization with microemulsion techniques: (i) scalable nanomanufacturing: nonsolvent, cost-effective synthesis of clearly established polyolefin nanoparticles. (ii) Thermal resilience: The functioning of elevated temperatures enables commercial compatibility without affecting·molecular weight control. (iii) Architectural precision: customized nanoparticle dimensions are achieved through the interaction of surfactants and catalysts, which facilitates the development of functional nanocarriers or catalytic templates. The following investigation redefines transition metal catalysis in polymer science, providing a sustainable method for the synthesis of sophisticated polyolefin nanomaterials with atomic-level precision.

In a significant study, Lin and Mecking[119] introduced a new series of phosphophenol nickel catalysts (**20e** and **20f**, Fig. 16) that were functionalized with hydrophilic sodium sulfonate substituents. The aforementioned catalysts, developed for aqueous-phase ethylene polymerization, address persistent issues in solvent-free polyolefin synthesis. Catalyst **20e** exhibited remarkable efficiency, facilitating ethylene polymerization promptly in water to produce low-molecular-weight polyethylene (M_n>6.1×10^4 g·mol^{-1}) under relatively mild conditions. This distinctive design avoids the use of volatile organic solvents (VOCs), which are typically required to solubilize a combination of catalysts and monomers. The end product, polyethylene, has a narrow molecular weight distribution, making it perfect for applications requiring uni-

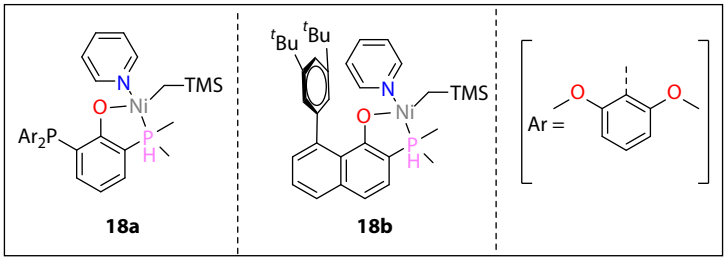

Fig. 15 SHOP Ni(II) catalysts with bulky phosphine-phenoxide ligand.[117]

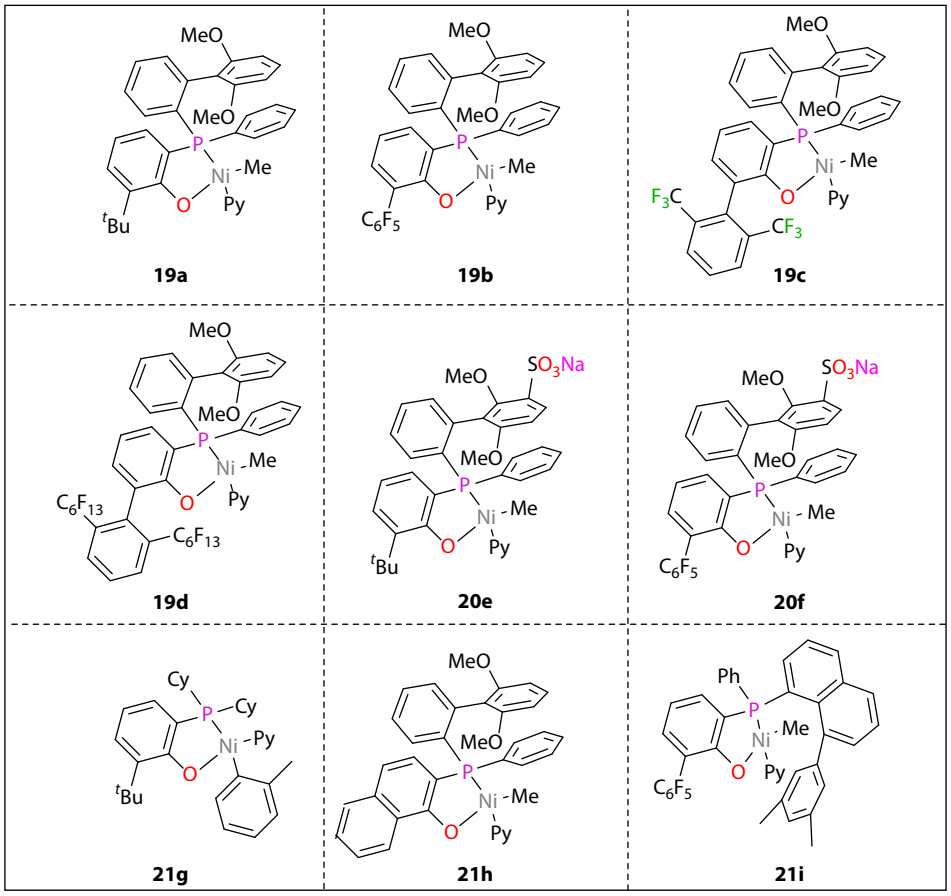

Fig. 16 Phosphine-phenolate Ni(II) complexes synthesized by Stefan Mecking.[31,118,119]

form coatings, such as corrosion-resistant films, in addition to packaging materials. The sodium sulfonate groups serve two purposes: (i) increasing water solubility by providing colloidal stability among the catalytic species, and (ii) hindering accumulation among the hydrophobic polymer chains during propagation. In particular, the aqueous polymerization method adheres to green chemistry principles by removing the solvent recovery processes and using less energy. The polymer's low M_n makes it easier to melt into thin, sticky coatings without thermal deterioration, which is a significant benefit over ultrahigh-molecular-weight polyethylenes, which are notoriously challenging to work with. The present investigation paves the door for a sustainable commercial polyolefin manufacturing process by proving the catalytic activity in water, especially for coatings and adhesives, where volatile organic compounds (VOCs) are a significant environmental and regulatory problem.

In recent years, more attention has been paid to circular and environmentally friendly economies. Polyethylene plastic has been rated as the worst invention of the 20th century owing to its non-degradable white pollution. Therefore, the closed-loop or upgraded recycling of polyolefin materials has gradually become a research hotspot. In 2021, Professor Stefan Mecking[31] discovered that the phosphine phenol nickel complex (Fig. 16, catalyst **19a**) can catalyze non alternating copolymerization of ethylene carbon monoxide (CO) with a CO insertion ratio of 1 mol%. In the resulting ketone PE material, the ketone groups were dispersed individually on the polymer backbone. After processing through traditional injection molding technology, the tensile properties of this ketone PE material were comparable to those of commercially available HDPE, and its photodegradation was confirmed by exposing the ketone PE film to simulated sunlight. In addition, catalysts **19d** and **21g**–**21i** (Fig. 16) achieved non alternating copolymerization of ethylene CO. This study demonstrates the potential for the preparation of photodegradable polyolefin materials.

During 2022, Agapie and co-workers[120] successfully developed a series of sterically demanding SHOP-type nickel catalysts (**22a**–**22f**) by implementing methylene-bridged phosphine-oxygen (P-O) donor ligands to thoroughly investigate the ligand architecture effects (Fig. 17). The conceptual framework utilizes bulky phosphine substituents to shield the asymmetrical positions of the nickel center, creating a shielding "sandwich" geometry that inhibits β-hydride elimination, which is a significant limitation in elevated temperature olefin polymerization. With regard to the catalysts tested, **22d** had the highest polyethylene molecular weights together with the largest steric bulk, providing direct evidence of a correlation between the ligand steric requirement and chain propagation efficiency. Interestingly, these systems also made it possible to copolymerize ethylene and tert-butyl acrylate, resulting in polyethylenes functionalized with ester groups. Catalyst **22d** exhibited remarkable activity (2.1×10^3 $g{\cdot}mol_{Ni}^{-1}{\cdot}h^{-1}$ at 90 °C), effectively tackling persistent issues of low copolymerization effective performance and thermal in-

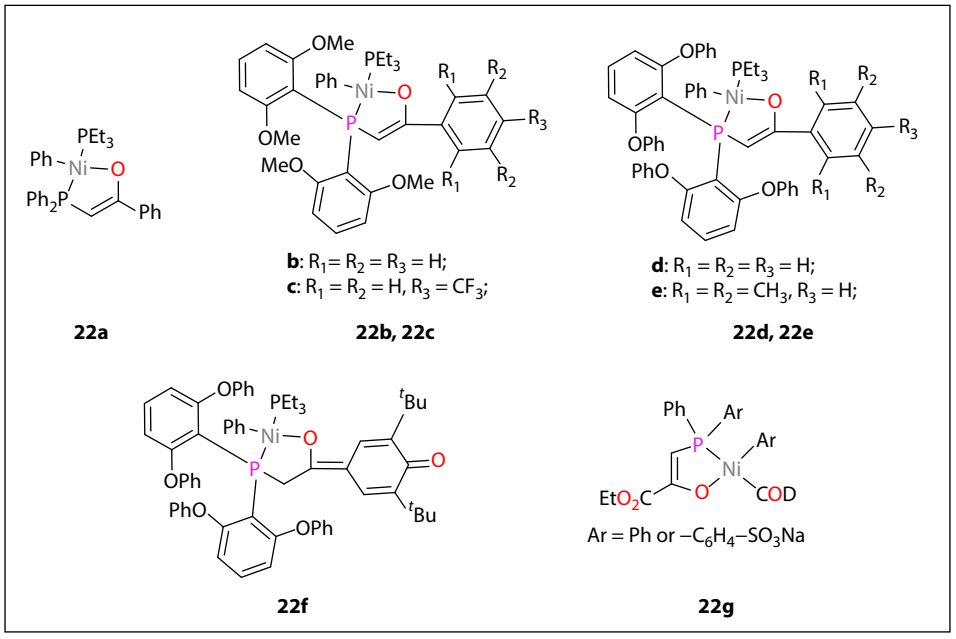

Fig. 17 SHOP Ni(II) catalysts with large phosphine substituents.[36,120]

stability in SHOP-catalyzed polar monomer incorporation. The present research demonstrates that steric engineering of ligand scaffolds is an innovative approach for the synthesis of high-value functional polyolefins under conditions pertinent to industrial applications.

Recently, our group[36] designed and characterized the heterogenization of homogeneous shell higher olefin process (SHOP) catalysts for the industrial production of linear low-carbon *α*-olefins from ethylene (Fig. 17, catalyst **22g**). By incorporating hydrogen-bonding interactions and ionic anchoring strategies, we functionalized SHOP nickel complexes with sodium sulfonate groups, creating heterogeneous catalysts that exhibited enhanced catalytic activity, higher polymer molecular weights, and narrower polydispersities compared to the original homogeneous catalysts. The heterogenization of SHOP-type nickel catalysts *via* sodium-sulfonate anchoring groups and solid supports like MgO, marks a significant advancement in polyolefin production, offering enhanced thermal stability (up to 150 °C), higher molecular weight polymers, and narrow polydispersity. Future efforts could focus on optimizing catalyst-support interactions by exploring advanced supports (*e.g.*, MOFs and graphene) or alternative anchoring strategies to improve stability and recyclability, while industrial scalability may benefit from continuous polymerization processes leveraging the catalysts' single-site behavior and fouling resistance. Expanding copolymerization with polar monomers could yield functionalized polyolefins for niche applications, and mechanistic studies using spectroscopy or DFT could reveal support-driven electronic modulation and deactivation pathways. Sustainability initiatives, such as reducing cocatalyst dependency and enabling catalyst recycling, along with lifecycle assessments against conventional systems, are critical for eco-conscious adoption. These modified catalysts demonstrate superior performance in ethylene polymerization, making them promising for the efficient production of highly crystalline linear *α*-olefins. These findings suggest that adopting heterogeneous catalytic systems could improve polyolefin production in industrial settings, offering benefits such as better catalyst stability and precise control over polymer properties. Challenges such as catalyst leaching, cost-effective ligand synthesis, and regulatory compliance with nickel usage must be addressed to fully realize their industrial potential. By bridging homogeneous precision with heterogeneous practicality, these systems promise to revolutionize polyolefin manufacturing, enabling tailored materials for high-performance applications, while advancing sustainable polymer synthesis. Future work could focus on further optimizing these systems to achieve greater efficiency and scalability in large-scale commercial applications. The collective advances highlight the adaptability of SHOP-Type catalysts in modifying polymerization pathways and polymer properties through precise control illustrated in Table 2, and summarized in Fig. 18.

5 MODIFIED IMINOPYRIDYL-BASED NICKEL AND PALLADIUM CATALYSTS

Building on early diimine-based systems, pyridine-imine ligands have surfaced as a unique category of unsymmetrical *α*-diimine frameworks, characterized by their distinctive electronic properties and steric adaptability. Nickel and palladium complexes with these ligands demonstrate remarkable catalytic efficiency in ethylene oligomerization, selectively producing low-molecular-weight branched polyethylene (M_n<10^3 g·mol^{-1}) or oligomers with microstructures optimized for lubricant applications. The aforementioned notable benefit of scalable commercial production is that pyridine-imine nickel catalysts are prepared *via* a simplified one-pot condensation of aniline derivatives, which results in high-yielding ligand synthesis (>90%) with little follow-up processing. The proposed thermal stability and regiocontrol have been significantly improved over the last 20 years owing to strategic alterations such as the addition of ortho-substituted aryl groups to the imine moiety (Fig. 19). This allowed for exact manipulation of the branching density and chain termination paths. These advancements highlight the pyridine

Table 2 Olefin polymerizations by various SHOP-type catalysts. [a]

Entry	Cat.	T (°C)	Yield [b] (g)	Act. [b]	M_n [c]	T_m [c] (°C)	CM [d]	Ref.
1	**12**	70	2.8	390	2.0	118.2	1.1	[113]
2	**13**	90	16.7	10020	9.4	129	25.5	[114]
3	**14**	80	1.2	0.5	23.4	2.0	91	[115]
4	**15**	40	0.42	0.8	3700	1.59	–	[116]
5	**16**	100	8.2	82	19.1	68.4	–	[117]
6	**17**	70	9.35	0.8	1955	146/139	78	[118]
7	**18**	70	3.97	2.0	6.1	137	62	[119]
8	**19**	100	1.13	1.4	60	133	1.7	[31]
9	**20**	90	2.1	1.0	10.9	122	0.6	[120]

Polymerization conditions: [a] toluene as the solvent and $AlEt_2Cl$ as the cocatalyst. [b] The yields and activities are averages of at least two runs. The activity was in units of 10^6 g·mol^{-1}·h^{-1}. [c] M_n is 10^4 g·mol^{-1} and was determined by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C with polystyrene standards. [d] Branching numbers per 1000C were determined by ^{1}H-NMR spectroscopy.

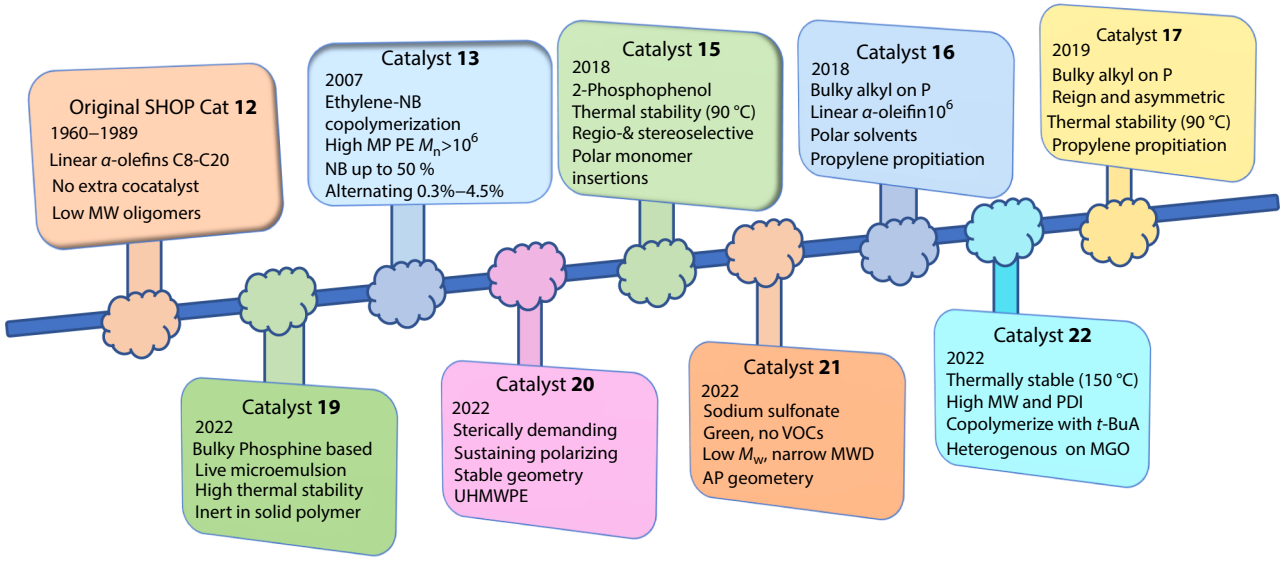

Fig. 18 Evolutionary roadmap of nickel phosphine catalyst design and application. A chronological overview illustrating the shift in catalytic capability *via* ligand modulation. Early systems (1960–1989) focused on low molecular weight oligomers, while mid-period advancements (2007–2018) targeted thermal stability and linear *α*-olefin control. Recent generations (2022) emphasize sterically demanding geometries for UHMWPE synthesis, live microemulsion techniques, and the incorporation of sodium sulfonate groups for VOC-free, green polymerization environments.

imine infrastructure as a versatile and synthetically accessible platform for the design of high-performance catalysts that connect academic innovation with industrial polyolefin manufacturing processes.

For instance, Laine and co-workers[37,123,124] designed that a series of dimeric pyridyl-imino nickel catalysts **23a** with different substituents have been shown to be active in ethylene polymerization[125], generating nearly linear or primarily methyl-branched polyethylenes with molecular weights of less than 3500 g·mol^{-1} at temperatures higher than 20 °C. In addition, pyridyl-imino palladium complexes **23b** activated by MAO showed high activity in the polymerization of bicyclo[2.2.1]hept-2-ene(norbornene)[125]. In 2012, Sun and co-workers[126] installed a large steric hindrance diphenylmethyl substituent on the pyridine imine ligand with different substituents (R_2 = H, Me) (Fig. 19), which increased the activity of catalyst **24** to 1.39×10^7 g·mol$_{Ni}^{-1}$·h^{-1}, but only produced branched polyethylene with a relatively low molecular weight (M_n<1000 g·mol^{-1}). The research group also installed a large steric hindrance substituent synthesis catalyst **24** on the other side of the ligand skeleton, which catalyzed the polymerization of ethylene to obtain low-molecular-weight oligomers. The sterically bulky C24 remained highly active toward ethylene polymerization (about 10^6 g$_{PE}$·mol$_{Ni}^{-1}$·h^{-1})[127], but the obtained polyethylenes were short-chain oligomers. Pyridine imine nickel catalysts with other ligand structures also exhibit similar polymerization properties.

Recently, Gao and co-workers[128] characterized a family of pyridine-imine palladium complexes with sterically demanding ortho-dibenzhydryl substituents. Cationic palladium catalysts exhibit dual functionality, facilitating ethylene oligomerization with significant activity while selectively producing highly branched oligomers (M_n = 600–800 g·mol^{-1}) with ultra-narrow polydispersity (PDI=1.03–1.12). The proposed advantageous incorporation of bulky ortho-dibenzhydryl groups boosted the thermal stability and catalytic efficiency while increasing the oligomer molecular weights, which is essential for applications that require precise control over branching and chain uniformity. Mechanistic studies indicated that steric bulk inhibits *β*-hydride elimination and chain-transfer path-

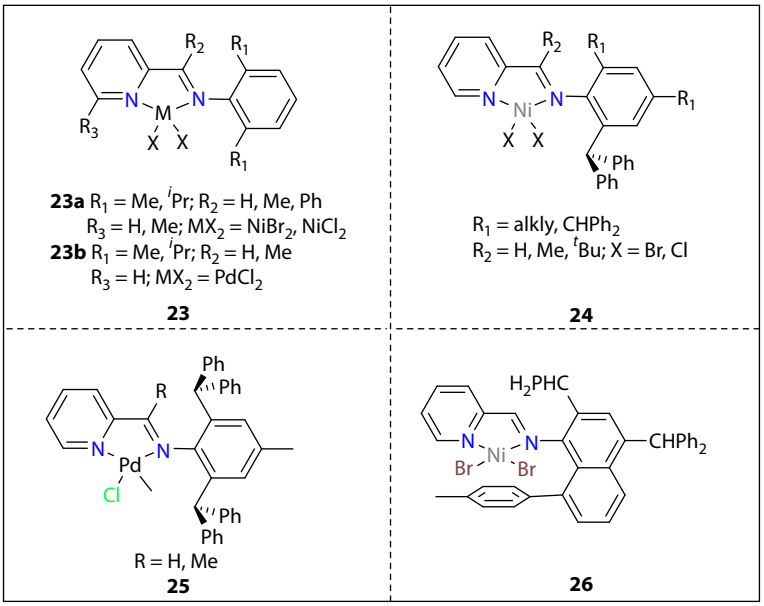

Fig. 19 Pyridinylimine-based nickel and palladium complexes.[37,123–126,128,129]

ways, thereby promoting propagation steps that produce well-defined oligomeric structures. This study emphasizes the significance of steric engineering in the design of palladium catalysts to overcome the persistent challenges in selective oligomerization, which may have implications for the synthesis of customized polyolefins in the lubricant and plasticizer sectors.

In 2016, Chen and co-workers[130] developed a new class of pyridine-imine nickel catalysts characterized by a "sandwich-like" ligand architecture that incorporates dual steric hindrance from the dibenzhydryl and naphthyl groups (Catalyst **26**, Fig. 19). The developed structure facilitated remarkable ethylene polymerization activity (4.3×10^6 $g_{PE}\cdot mol_{Ni}^{-1}\cdot h^{-1}$), producing ultrahigh-molecular-weight polyethylene (M_w up to 1.43×10^6 $g\cdot mol^{-1}$) and semicrystalline poly(*α*-olefin)s with increased melting temperatures (T_m). The interaction between the dibenzhydryl and naphthyl groups improved thermal stability and inhibited chain-transfer pathways, which are specifically connected to the exceptional control over the molecular weight and the crystalline structure associated with the polymer. The results demonstrate the significant potential of sterically tailored dinuclear ligands for enhancing the precision of polyolefin synthesis, especially for applications requiring high thermal stability and mechanical strength, including industrial fibers and high-performance plastics.

Brookhart and co-workers[131] reported that 8-arylnaphthyl groups incorporated into pyridine-imine nickel catalysts **27** that block only a single axial site are highly effective in retarding chain transfer[46]. Comparing the associative ligand exchange rates in the palladium complexes, these aryl groups shielded the axial sites more effectively than the o-isopropyl groups. These complexes yield highly branched polyethylenes (*ca.* 30–90 branches per 1000 carbons) with good molecular weights of up to 2.6×10^4 $g\cdot mol^{-1}$. Compared to an ortho-disubstituted aryl imine moiety, the 8-arylnaphthyl group provides strong axial shielding for one axial site, which favors propagation over chain transfer.

In 2019, Rui and co-workers[132] synthesized a series of para-benzhydryl-substituted iminopyridyl-based nickel and palladium catalysts **28** (Fig. 20) for ethylene oligo-/polymerization. These nickel complexes demonstrated good thermal stability and high activity of up to 7.13×10^6 $g_{PE}\cdot mol_{Ni}^{-1}\cdot h^{-1}$, while the Pd(II) catalysts produced highly branched oligomers in high yields (up to 141 branches/1000C). The branching densities increased with increasing polymerization temperature and decreasing ligand bulkiness and could be tuned over a wide range of 95/1000C–141/1000C.

Pellechia and co-workers[133] conducted a thorough study of pyridine imine nickel catalysts (Fig. 20), indicating how strategic substituent changes to pyridine, along with amino moieties, improve catalytic activity. Catalyst **29** demonstrated dual functionality, facilitating both ethylene homopolymerization and copolymerization, along with methyl acrylate (MA), to produce hyperbranched oligomers. This system demonstrated significant control over the incorporation of polar monomers, with MA units integrated into the polymer chains through various insertion modes and adjustable ratios between 0.2 mol% and 35 mol%. The precise modulation of the branching topology along with the polar content underscores the potential of the catalyst for synthesizing functional polyolefins designed for specialty applications, including adhesives and compatibilizers. This study highlights the importance of ligand architecture in the development of nickel catalysts that can effectively tackle persistent issues in olefin-polar monomer copolymerization.

Under ambient circumstances, Sun and co-workers achieved productivities of up to 1.22×10^7 $g_{PE}\cdot mol_{Ni}^{-1}\cdot h^{-1}$ by modifying a family of iminopyridyl ligands based on naphthylamine. These complexes, shown in Fig. 20, associated with catalyst **30**, exhibit outstanding catalytic activity for ethylene polymerization[134]. A remarkable achievement for nickel-mediated polymerization at moderate temperatures is the selective generation of branching polyethylene with narrow poly-

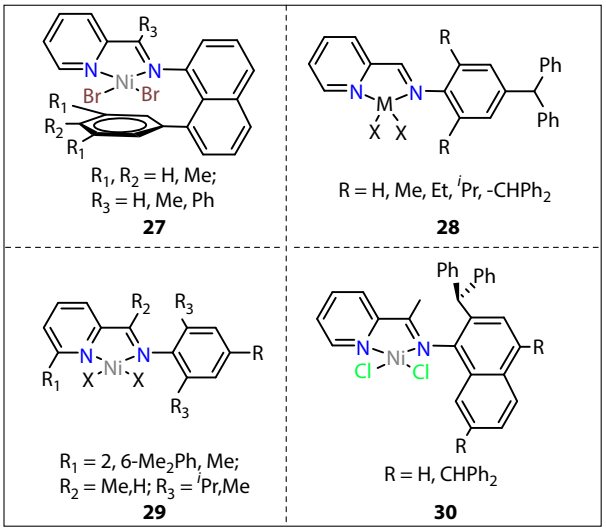

Fig. 20 [N, N] and [N, O] Ni(II) catalysts.[131–134]

dispersity indices (PDI) and ultra-low molecular weights (M_n < 500 g·mol^{-1}) by these systems. The precise control of the polymer architecture, resulting in short-chain branches and uniform chains, makes these catalysts strong candidates for industrial-scale production of polyethylene waxes and lubricants, where low M_n and customized branching are essential for performance. This study highlights the significance of ligand design in optimizing nickel catalysts to address issues in polyolefin functionalization and specialty polymer production.

In 2023, Dai and co-workers designed two complementary strategies namely, the "sandwich" and rotation-restricted approaches have been successfully employed in iminopyridyl Ni(II) and Pd(II) catalysts to suppress chain transfer reactions and access high-molecular-weight polyolefins (Fig. 21, catalyst **30a**).[139] A family of such complexes featuring flexible backbones and rigid axial bulky aryl substituents (dibenzosuberyl or 8-arylnaphthalenyl) was designed and evaluated. In ethylene polymerization, both Ni and Pd catalysts exhibited reasonable activities and produced highly branched polyethylenes with high molecular weights. The catalysts bearing dibenzosuberyl groups significantly outperformed their 8-arylnaphthalenyl counterparts in both activity and molecular weight enhancement. This trend extended to palladium-catalyzed ethylene–methyl acrylate copolymerization, where the dibenzosuberyl system yielded higher-molecular-weight copolymers. Importantly, both Pd catalysts enabled the production of highly branched E-MA copolymers with moderate-to-high molecular weights and remarkably high MA incorporation ratios (up to 17.4 mol%). Most strikingly, relative to conventional dibenzhydryl catalysts, these strategically designed iminopyridyl systems demonstrated a superior capacity to retard chain transfer, affording polymers and copolymers with molecular weights one to two orders of magnitude higher, underscoring the efficacy of these dual strategies in accessing high-molecular-weight, highly branched polyolefin materials.

In the same year, the same group synthesized and characterized a series of rigid–flexible double-layer steric iminopyridyl Ni(II) and Pd(II) complexes, incorporating bulky dibenzhydryl groups with remote 4-cycloalkyl or -phenyl substituents for ethylene (co)oligomerization (Fig. 21, Catalyst **30b**).[140] These catalysts demonstrate high efficiencies in environmentally benign alkane solvents, offering advantages over traditional aromatic media for industrial applications. Notably, the flexible catalysts bearing remote cyclohexyl substituents outperformed their rigid–rigid phenyl-substituted analogs, exhibiting higher activities and producing ethylene oligomers with increased molecular weights. The resulting ethylene oligomers and co-oligomers featured hyperbranched microstructures, highlighting the potential of this catalyst design for accessing novel polyolefin architectures

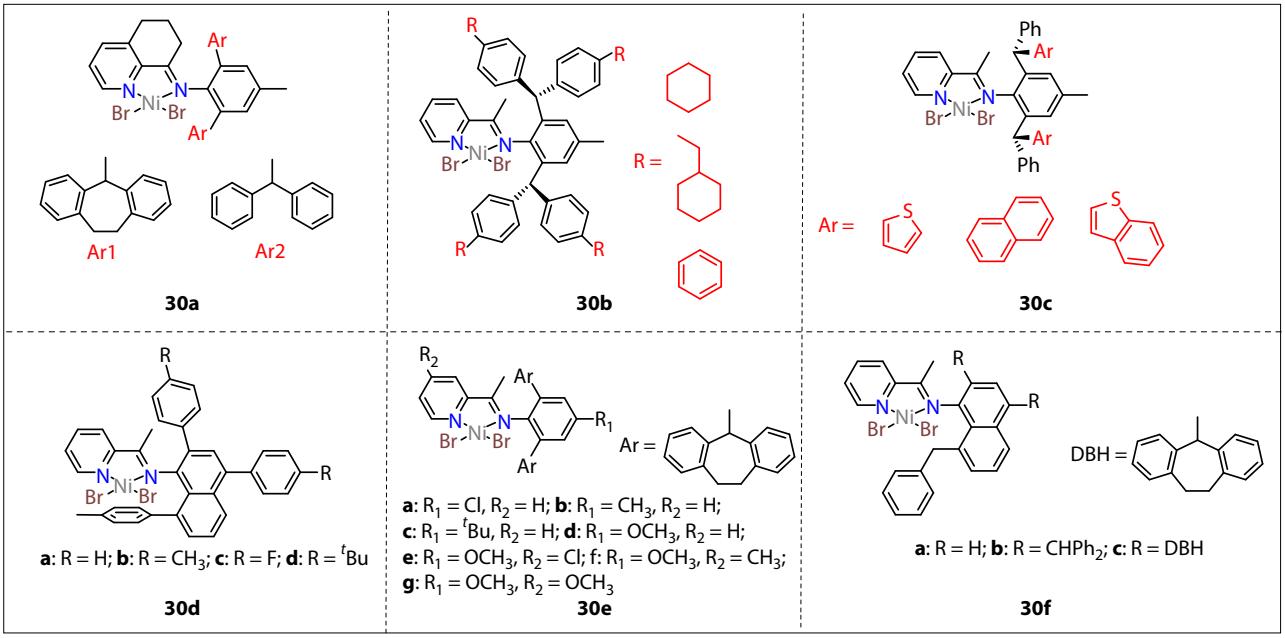

Fig. 21 Iminopyridyl Ni(II) catalysts.[139–144]

under industrially relevant conditions.

In 2023, Dai and co-workers[141] developed three unsymmetrical arylamine-based pyridine imine ligands and their corresponding Ni(II) and Pd(II) complexes for ethylene oligomerization (Fig. 21, catalyst **30c**). The nickel complexes exhibit high activities (10^6 g·mol^{-1}·h^{-1}), producing highly branched (66/1000C–89/1000C) oligoethylenes with molecular weights of 1.4–3.2 kg·mol^{-1}, wherein methyl branching predominates. In contrast, the palladium analogs display moderate activities (10^4 g·mol^{-1}·h^{-1}) and yield lower molecular weight (0.4–0.6 kg·mol^{-1}) oligoethylenes with even higher branching densities (103/1000C–126/1000C), characterized by predominantly C3$^+$ branching. In ethylene–methyl acrylate co-oligomerization, the Pd complexes afford ester-functionalized oligoethylenes with high incorporation ratios (6.86 mol%–14.16 mol%) but low molecular weights (about 0.4 kg·mol^{-1}). All the oligoethylenes and functionalized derivatives produced exhibited hyperbranched architectures. Notably, compared to fully benzothiophene-substituted pyridine-imine catalysts, the partially substituted analogs demonstrated significantly higher activities and yielded much higher molecular weights of oligoethylenes, highlighting the critical influence of the ligand substitution pattern on catalytic performance.

In 2024, Dai and co-workers[142] designed a series of 2,4,8-triarylnaphthyl iminopyridyl nickel catalysts, capitalizing on the chain-walking strategy, to access polyethylene thermoplastic elastomers in a straightforward manner (Fig. 21, catalyst **30d**). These catalysts exhibit moderate activity (10^5 g·mol^{-1}·h^{-1}) and produce high-molecular-weight polyethylenes (up to 145.5 kg·mol^{-1}) with high branching densities (75/1000C–95/1000C) and correspondingly low melting points. Detailed microstructural analysis using ^{13}C-NMR revealed predominantly methyl and long-chain branches. Notably, the resulting materials demonstrate an exceptional combination of mechanical properties, including moderate stress at break (4.64–6.97 MPa) coupled with ultrahigh strain at break values (1650%–3752%), indicative of outstanding ductility and excellent elastic recovery (72%–85%).

In 2025, the same group[143] developed a novel class of nickel dibenzosuberyl iminopyridyl catalysts with variable backbones and arylamine electronic properties to address the processing challenges associated with high-molecular-weight polyolefin elastomers from traditional *α*-diimine systems (Fig. 21, catalyst **30e**). These catalysts exhibit high activities (10^6 g·mol^{-1}·h^{-1}) in ethylene polymerization and enable the synthesis of polyethylene elastomers with moderate, processable molecular weights (53.8–156.9 kg·mol^{-1}) and branching densities (55/1000C–87/1000C). While catalyst electronics exert a general influence on polymerization behavior, increasing the temperature significantly reduces activity and alters both molecular weight and branching density. The resulting elastomers demonstrated excellent mechanical properties, including high elongation at break (1617%–1729%), moderate tensile strength (5.46–10.58 MPa), and elastic recovery (30%–45%).

During the same year, the same group[144] synthesized a dual-axial-substituent strategy to address the fundamental challenge of controlling chain transfer in pyridine-imine Ni(II)- and Pd(II)-catalyzed ethylene (co)polymerization (Fig. 21, catalyst **30f**). A family of catalysts featuring both 8-benzhydryl and 2-diarylmethyl naphthylpyridine-iminate ligands was synthesized, wherein the cooperative shielding of both axial sites synergistically suppressed chain transfer. Ni catalysts activated with diethylaluminum chloride exhibit high activities (*ca.* 10^6 g·mol^{-1}·h^{-1}) and produce branched polyethylenes with molecular weights up to 246.4 kg·mol^{-1}, an order of magnitude higher than that of single-substituent controls. The Pd analogs yielded hyperbranched polyethylenes with M_n up to 43.8 kg·mol^{-1} and achieved outstanding methyl acrylate incorporation (up to 13 mol%) during copolymerizations while maintaining practical molecular weights (4.1–8.4 kg·mol^{-1}).

Dinuclear iminopyridyl Ni(II) and Pd(II) complexes (Fig. 22, catalysts **31a** and **31b**) have been successfully identified as effective catalysts for olefin transformations, utilizing potential cooperative interactions between neighboring metal centers to influence the reactivity and selectivity. Sun and co-workers developed methylene-bridged bis-iminopyridine dinickel catalysts (**31a**) the fact that upon activation with methyl aluminoxane (MAO), demonstrated significant activity in ethylene oligomerization and polymerization, resulting in the production of oligomer and polyethylene mixtures[135]. Both computational and experimental analyses identified Ni–Ni cooperativity as a crucial element in the distinctive performance of the catalyst, indicating synergistic electronic interactions between the two metal sites. As a follow-up to this study, Hu and co-workers performed vinyl addition polymerization of norbornene using bridged dinuclear diimine Ni/Pd complexes (**31b**).[136] The palladium variants demonstrated more desirable catalytic activity than their nickel counterparts, functioning through a single-site mechanism to produce polynorbornene copolymers characterized by improved packing density, thermal stability, and glass transition temperatures (in comparison to polystyrene), as well as broadened solubility and processability relative to traditional polynorbornene. Solan and co-workers extended this structural paradigm by synthesizing an aryl-bridged pyridine-imine palladium complex (catalyst **34**) for ethylene oligomerization.[145] The approach exhibited moderate activity and succeeded in primarily yielding low-molecular-weight polyethylene characterized by methyl-branched microstructures, in contrast to the linear architectures commonly associated with nickel-based analogs. The collective advances highlight the adaptability of dinuclear architectures in modifying polymerization routes, in addition to properties, by precisely controlling metal nuclearity, ligand geometry, and intermetallic interactions.

Chen and co-workers[137] synthesized xanthene-bridged dinuclear nickel complexes (catalyst **35**, Fig. 23) that incorporate dual bromide-linked Ni centers as part of a structured bis-iminopyridyl framework. Following stimulation with methyl aluminoxane (MAO), the aforementioned dinuclear systems demonstrated enhanced catalytic activities (up to 2.4×10^6 g_{PE}·mol_{Ni}^{-1}·h^{-1}) for ethylene polymerization, surpassing mononuclear analogs in terms of productivity as well as polymer characteristics. The catalysts generated polyethylene, characterized by substantially elevated molecular

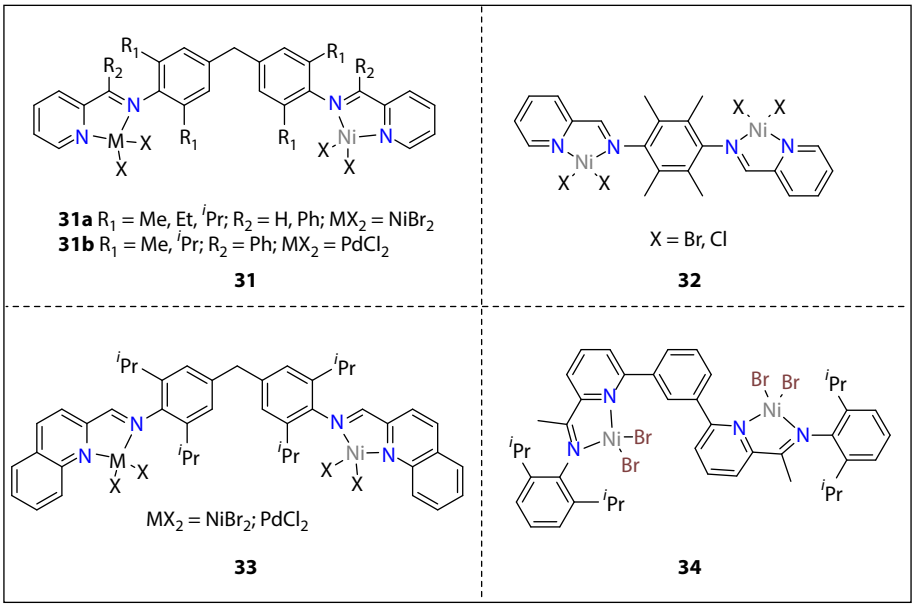

Fig. 22 Structures of bridged di-nuclear diimine nickel and palladium complexes.[135,136,145,146]

weights and notably diminished branching densities (27 branches per 1000 carbons), representing a significant advancement for applications requiring linear, high-strength polyethylenes. This significant difference from mononuclear systems highlights the crucial function of the xanthene bridge in stabilizing cooperative intermetallic interactions, which somewhat inhibits chain-transfer pathways while improving regiocontrol through propagation. The present research establishes dinuclear architectures as an effective strategy for modifying polymerization kinetics along with the polymer microstructure, thereby facilitating the precise design of industrial polyolefins.

Meyer and co-workers designed a series of pyrazolate-based di-nuclear nickel and palladium complexes catalysts **36** (Fig. 24) with appended arylimino side arms[138]. The di-nuclear nickel complex catalyst **36a** activated by MAO showed high activity in ethylene polymerization and was significantly more active than the corresponding palladium systems (catalyst **36b**), similar to the observations for the mononuclear catalysts. The microstructures of the polyethylenes (total branching, T_m and molecular weights) obtained using catalyst **36a** are similar to those reported previously for mononuclear classic *α*-diimine nickel complexes. In addition, Ess and co-workers synthesized a naphthyridine-diimine di-nuclear nickel complex, where catalyst **37** catalyzed the selective cyclotrimerization of monosubstituted alkynes, whereas mononuclear Ni catalysts generally give cyclotetramerization of alkynes.[66]

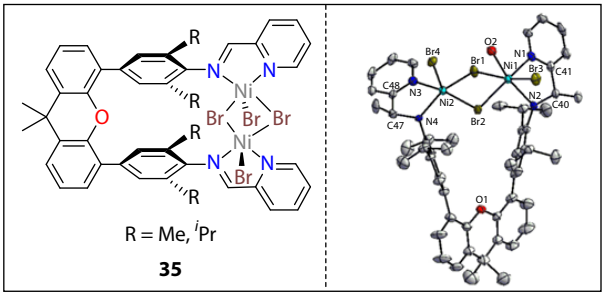

Fig. 23 Xanthene-bridged iminopyridyl di-nuclear nickel complexes.[137]

A series of diarylmethyl-substituted iminopyridine palladium(II) catalysts with high steric resistance was synthesized. The four catalysts showed high TOF values (up to 1.1×10^4 h^{-1}) and high thermal stability (half-life > 12 h) in ethylene oligomerization, and hyperbranched ethylene oligomers were pro-

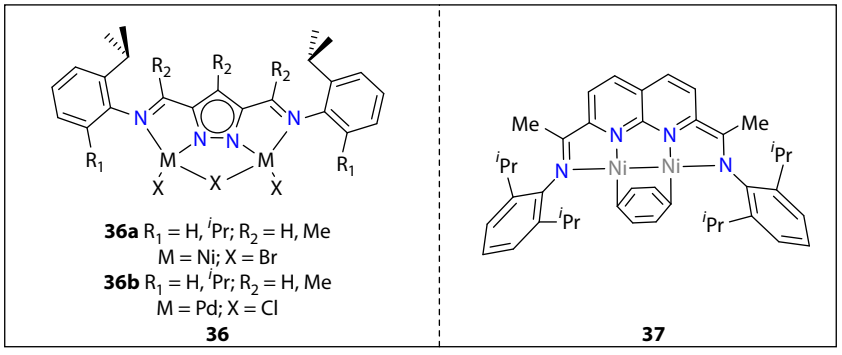

Fig. 24 Pyrazolate- and naphthyridine-based di-nuclear diimine nickel and palladium complexes.[66,138]

duced. In ethylene–MA co-oligomerization, hyperbranched polar functional ethylene oligomers with very high incorporation (up to 15%) were obtained, which are expected to have potential applications as viscosity modifiers or interface active agents. Remarkably, the preparation of polar functional ethylene oligomers involves only one step with a low catalyst loading, which is somewhat in agreement with the concept of green chemistry. In terms of the catalysts, the remote non-conjugated electronic substituents of the bulky diarylmethyl moiety in these catalysts have a pronounced impact on the ethylene (co)oligomerization. The electron-donating substituents improved the molecular weight and decreased the branching density of the resulting ethylene oligomers and ethylene–MA cooligomers. Moreover, electron-donating substituents can enhance the incorporation of MA in ethylene–MA co oligomerization. The structural design principles and representative catalyst architectures are illustrated in Table 3 and summarized in Fig. 25.

6 OTHER NICKEL CATALYTIC SYSTEMS

The progress in olefin polymerization catalysts is fundamental to industrial polymer research, supporting the creation of materials essential to industries such as packaging and car manufacturing. The past few decades have seen significant advancements in catalyst design, propelled by innovative research on ligand architectural designs. Most significantly, novel methodologies in ligand synthesis, as shown by the work of Refs. [31] and [147], have widened the frontiers of catalytic accomplishments, permitting precise control over the polymer microstructure and molecular weight distributions. An exhaustive examination of these advancements identifies three essential design principles that support high-performance catalysts: (i) multisite regulation, which promotes cooperative interactions among diverse active sites to improve stereochemical control; (ii) electronic asymmetry, which establishes customized microenvironments to influence reactivity and selectivity; and (iii) rigid ligand frameworks, which ensure structural stability while inhibiting unproductive coordination modes. These concepts jointly address enduring issues in chain propagation, comonomer integration, and temperature stability. Although group 4 metallocene and late-transition-metal complexes have predominated recently, nickel-based catalysts have surfaced as persuasive yet insufficiently investigated alternatives. Their abundance on Earth, adjustable redox characteristics, and distinct ability for chain-walking processes make them suitable candidates for copolymerizing difficult substrates such as polar monomers or strained olefins. A thorough examination of nickel catalysts, especially those utilizing previously indicated design principles, is lacking in the most recent literature. This section addresses this gap, clarifying how selective ligand changes in nickel systems can reveal novel catalytic behaviors and provide insights into structure-activity connections beyond conventional metallocene paradigms. Through the integration of mechanistic research and kinetic assessments, we elucidated strategies to overcome the constraints in activity and stability, thereby promoting the sustainable synthesis of next-generation polyolefins.

6.1 Phosphine-nickel Phosphonimide Catalyst

In 2018, Chen and co-workers[148] introduced an innovative class of cationic nickel catalysts based on fundamental investigations of phosphine-phosphonimide ligand structures[149–151] (Fig. 26).[94] These catalysts possess a modular ligand structure with three independently adjustable sites, which facilitates the precise regulation of the steric, electronic, and coordination dynamics during polymerization. The aforementioned multisite regulatory approach facilitates the systematic enhancement of catalytic activity, comonomer integration, and polymer microstructure. Catalyst **38**, a prominent member of this family, has remarkable ethylene polymerization activity (3.6×10^6 g·mol$_{Ni}^{-1}$·h^{-1}), comparable to advanced late-transition-metal systems. This platform enables the copolymerization of ethylene with difficult polar and functionalized monomers, such as long-chain alkyl esters (*e.g.*, 10-undecenoate), chloroalkenes, and 4-pentene-1-yl acetate. These reactions occur with remarkable catalytic efficiency (2.5–150 kg·mol$_{Ni}^{-1}$·h^{-1}), while exhibiting low comonomer incorporation (0.2 mol%–3.3 mol%) and yielding polymers with adjustable molecular weights (1200–27000 g·mol^{-1}). The inhibited β-hydride elimination, due to the ligand's inflexible, electron-asymmetric structure, improves chain propagation efficiency and facilitates the production of narrowly distributed oligomers and functional polyolefins. This study illustrates the efficacy of multisite ligand design in resolving enduring trade-offs among activity, selectivity, and polymer characteristics. The capacity to customize the catalyst performance by specific structural alterations underscores

Table 3 α-Olefin polymerizations by pyridinylimine-based nickel and palladium catalysts.[a]

Entry	Cat.	T (°C)	Yield (g)	Act.[b]	M_n[c]	PDI[c]	B[d]	Ref.
1	**23**	20	7.08	57.00	2.2	24.0	113.3	[125]
2	**24**	20	15.5	9.30	2.00	103	63.1	[126]
3	**25**	45	7.94	99.3	75.1	1.12	116	[128]
4	**26**	–20	6.41	16.0	142.5	1.43	25	[130]
5	**27**	25	3.8	38.0	2.6	1.9	49	[131]
6	**28**	60	7.13	5.70	3.52	2.31	124	[132]
7	**29**	40	0.10		0.3	1.0	18	[133]
8	**30**	30	1.22	12.2	13.0	2.11	59.2	[134]
9	**31**	20	32.8	32.8	15.40	–	–	[135]
10	**32**	30	0.6	20.6	–	–	–	[136]
11	**34**	20	4.22	16.88	24.00	2.8	27	[137]
12	**35**	18	1.47	23.5	3.7	2.7	51	[138]

Polymerization conditions: [a] toluene as the solvent and $AlEt_2Cl$ as the cocatalyst; [b] The yields and activities are averages of at least two runs. The activity was in units of 10^6 g·mol^{-1}·h^{-1}. [c] M_n is 10^4 g·mol^{-1} and was determined by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C with polystyrene standards. [d] Branching numbers per 1000C were determined by ^{1}H-NMR spectroscopy.

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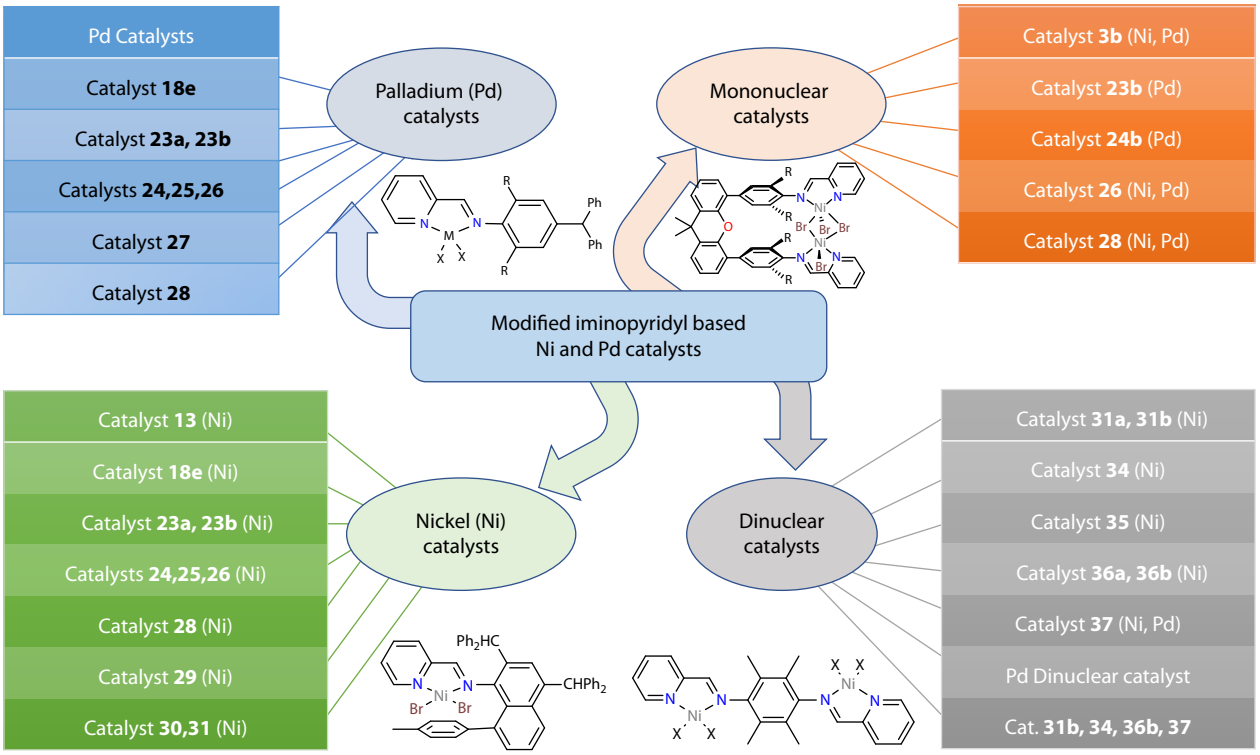


Fig. 25 Flow chart for modified Iminopyridyl based Ni and Pd catalysts. Structural classification and library of modified iminopyridyl-based Ni and Pd catalysts. The flowchart illustrates the divergent design strategies for iminopyridyl catalysts, categorized by metal center and nuclearity. (Left) Mononuclear systems are divided into palladium (Pd) and nickel (Ni) complexes, highlighting the evolution from simple derivatives (Cat. **18e**, **23a**/**23b**) to sterically bulky diarylmethyl-substituted and imidoyl-arene spacer systems designed to modulate polymerization activity and polymer branching. (Right) Classification based on nuclearity, distinguishing between structurally defined mononuclear species and dinuclear complexes (Cats. **31**–**37**). These multinuclear systems utilize bridging frameworks to exploit cooperative metal-metal effects, potentially enhancing thermal stability and control over polyethylene architecture. Representative 2D chemical structures highlight the core coordination environments and the modular nature of the ligand backbone.

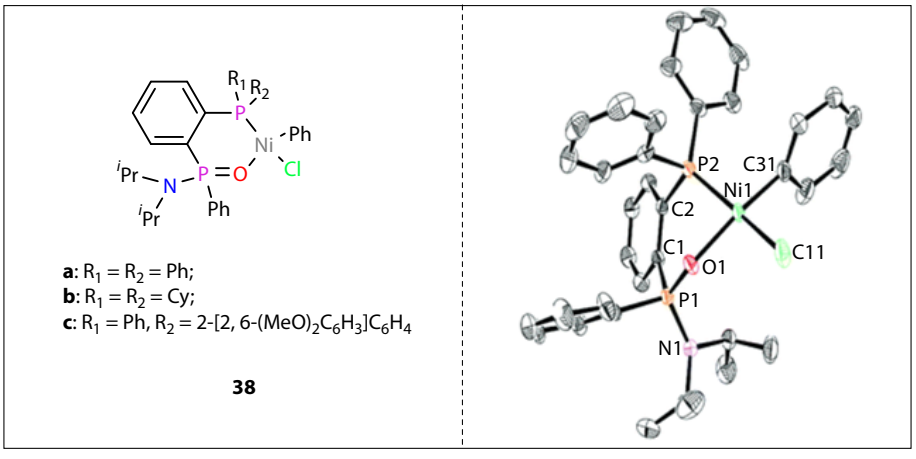
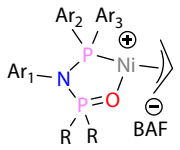


Fig. 26 PPO Ni(II) catalysts prepared by Chen *et al.*[148]

the adaptability of nickel in producing specialized polyolefins, ranging from low-molecular-weight waxes to polar-functionalized copolymers. These improvements highlight Ni-based systems as a viable platform for sustainable polymer chemistry, connecting academic innovation with industrial scalability.

6.2 Phosphine Nitride Phosphine Nickel Oxide Catalyst

By introducing a groundbreaking phosphine-nitrogen-phosphine oxide (PNPO) ligand design in 2018, Chen and co-workers synthesized Pd and Ni catalysts with previously unheard levels of electronic and steric tunability (Fig. 27, catalyst **39**)[152]. The PNPO framework uniquely combines a robust σ-donor phosphine moiety with a weak *σ*-donor phosphine oxide group, establishing an inherent electrical asymmetry that optimizes the metal center reactivity. This approach enables multi-site ligand modulation, allowing for separate adjustments of the steric bulk, donor strength, and coordination geometry to regulate



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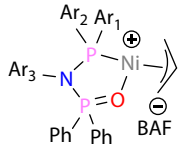
a: R = Ar_1 = Ph, Ar_2 = Ar_3 = 2-MeO-C_6H_4;
b: R = Ar_1 = Ar_2 = Ph;
c: R = ^{i}Pr, Ar_1 = Ar_2 = Ph;
d: R = Ph, Ar_1 = 4-MeO-C_6H_4, Ar_2 = Ph;
e: R = Ph, Ar_1 = 4-CF3-C_6H_4, Ar_2 = Ph



40

a: Ar_1 = Ph, Ar_2 = 2-[2,6-$(MeO)_2C_6H_3$]C_6H_4, Ar_3 = 4-Me_2N-C_6H_4;
b: Ar_1 = Ph, Ar_2 = 2-[2,6-$(MeO)_2C_6H_3$]C_6H_4, Ar_3 = 4-MeO-C_6H_4;
c: Ar_1 = Ph, Ar_2 = 2-[2,6-$(MeO)_2C_6H_3$]C_6H_4, Ar_3 = Ph;
d: Ar_1 = Ph, Ar_2 = 2-[2,6-$(MeO)_2C_6H_3$]C_6H_4, Ar_3 = 4-CF_3-C_6H_4;
e: Ar_1 = Ar_2 = 2,6-$(MeO)_2C_6H_3$, Ar_3 = 4-Me_2N-C_6H_4;
f: Ar_1 = Ar_2 = 2-MeO-C_6H_4, Ar_3 = 4-Me_2N-C_6H_4;
g: Ar_1 = Ar_2 = Ph, Ar_3 = 4-Me_2N-C_6H_4;
h: Ar_1 = Ar_2 = 2-CF_3-C_6H_4, Ar_3 = 4-Me_2N-C_6H_4;
i: Ar_1 = Ar_2 = 4-MeO-C_6H_4, Ar_3 = 4-Me_2N-C_6H_4;
j: Ar_1 = Ar_2 = 4-CF_3-C_6H_4, Ar_3 = 4-Me_2N-C_6H_4;

Fig. 27 PNPO Ni(II) catalysts.[152,154]

the polymer microstructure, molecular weight, and comonomer insertion. The principal benefits of the PNPO system include: (i) Electronic Asymmetry: the contrast between robust (P) and feeble (P═O) σ-donors creates a polarized metal milieu, augmenting oxidative stability, and inhibiting chain-transfer mechanisms. (ii) Dual-Metal Versatility: Both palladium and nickel variations effectively accelerate the production of ester-functionalized polar polyolefins under moderate conditions (25–60 °C, < 2 MPa ethylene), surpassing conventional constraints in polar monomer compatibility. (iii) Mechanistic Divergence: PNPO-Pd catalysts facilitate non-alternating ethylene/CO copolymerization,[153] whereas PNPO-Ni systems induce alternating copolymerization,[154] underscoring ligand-controlled regioselectivity. In 2022, Liu and co-workers[154] developed a series of cationic PNPO-Ni catalysts, optimizing their electronic contributions through substituent effects. Catalyst **40e**, which incorporates electron-donating groups, achieved complete alternation in ethylene/CO copolymerization, resulting in ultrahigh-molecular-weight poly ketones (M_n = 1.5×10^6 g·mol^{-1})—a 15-fold enhancement compared to previous systems. This advancement highlights the importance of ligand electron richness in stabilizing propagating chains and reducing β-hydride elimination. The PNPO ligand framework illustrates the potential of electronic and steric engineering to achieve dual functionality: Pd systems enhance the accessibility of polar-functionalized polyolefins, whereas nickel catalysts facilitate the scalable synthesis of engineering-grade polyketones. PNPO-based catalysts serve as essential instruments for the progress of sustainable polymer chemistry, connecting academic advancements with industrial requirements for high-performance materials.

6.3 Naphthoquinone Imide Nickel Catalyst

In 2017, Cai and co-workers[155] introduced a novel class of nickel catalysts featuring naphthoquinone imide (NQI) ligands, addressing significant issues related to thermal stability and polar monomer copolymerization. The diphenylmethyl-substituted NQI-Ni variant exhibited remarkable ethylene polymerization activity (10^6 g·mol_{Ni}^{-1}·h^{-1}) while yielding polyethylenes with adjustable molecular weights (M_n = 700–2.2×10^5 g·mol^{-1}). This extensive molecular weight distribution, ranging from oligomers to high polymers, underscores the capacity of the ligand to influence the chain-transfer kinetics *via* steric and electronic effects. The catalyst facilitated the copolymerization of ethylene with polar monomers, including 5-hexene-1-yl ester, but with restricted incorporation (≤1.6 mol%). This insertion rate indicates ongoing difficulties in polar monomer activation, although the ability of the system to maintain activity under these circumstances highlights the resilience of the NQI scaffold to Lewis basic poisoning, a frequent constraint in late-transition-metal catalysis. A significant novelty was found in the non-coordinating carbonyl group of catalyst **41**, which formed hydrogen bonds with methyl aluminoxane (MAO)-modified SiO_2 substrates. This interaction enabled the formation of a hetero phase catalyst system, significantly increasing heat stability (up to 80°C) and boosting polymer morphology by inhibiting agglomeration. The hydrogen-bonding mechanism represents a transformative approach for catalyst immobilization, avoiding conventional covalent anchoring techniques that frequently hinder active-site accessibility. This study enhances nickel catalysis for industrial applications by integrating ligand design with supramolecular stabilization. The resilience of the heterophase system at high temperatures and its capacity to generate free-flowing polymer granules tackle significant scaling challenges in slurry- and gas-phase reactors. The adaptability of the NQI platform encourages further investigation of customized hydrogen-bonding motifs to enhance the integration of polar monomers, thereby connecting academic research with sustainable manufacturing of functional polyolefins. The representative catalyst structures and their structure–property relationships are summarized in Fig. 28.

6.4 Nickel Carbonyl Imide Catalyst

In groundbreaking 2020 work, Chen and co-workers introduced a simple yet highly effective α-ketoimide ligand platform (Fig. 29), which was developed as a synthetic intermediate in the synthesis of α-diimides[156]. When coupled with a cationic [Ni(al-

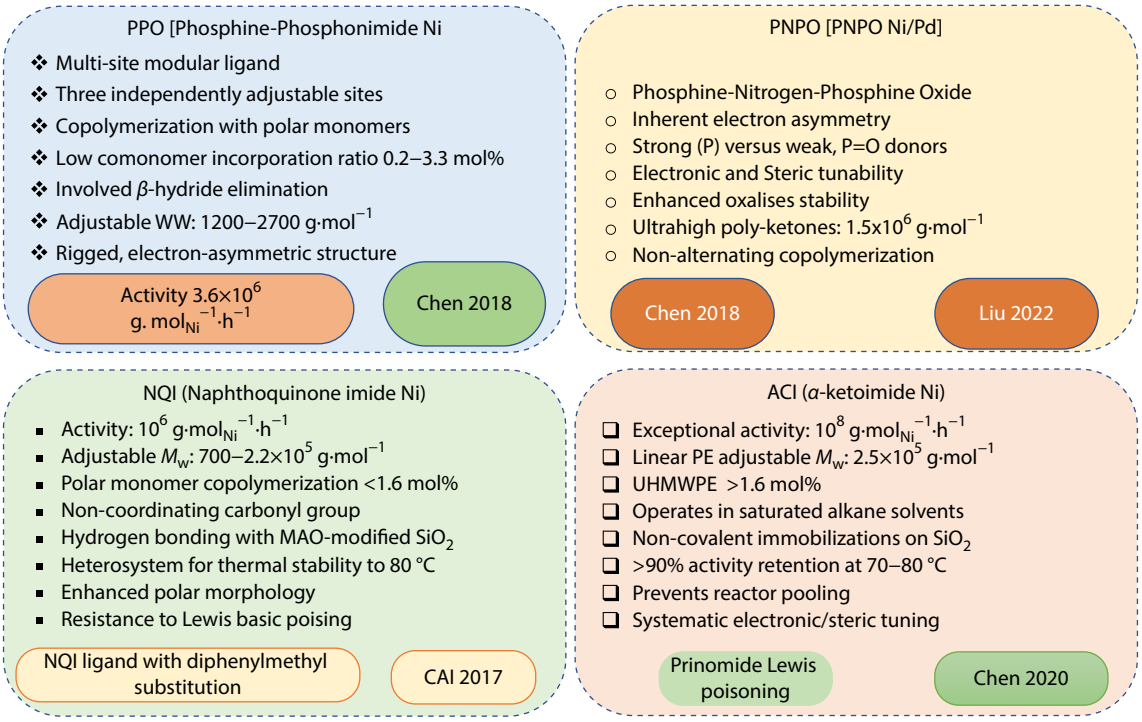


Fig. 28 Key features and catalytic performance of PPO, PNPO, NQI, and ACI-based Ni/Pd catalysts. Highlights include the high activity of ACI systems (10^8), the structural modularity of PPO ligands, the oxidative stability of PNPO complexes, and the heterosystem thermal stability provided by NQI frameworks. These systems represent milestones in the development of late-transition metal catalysts for high-value-added polyethylene and polar copolymers.

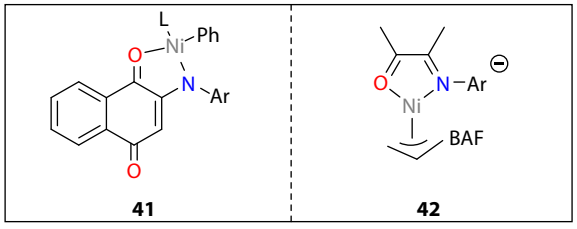


Fig. 29 [N, N] and [N, O] Ni(II) catalysts.[155,156]

lyl)]$^+$ precursor, the carbonyl-imine ligand produces single-site nickel catalysts (**42**) that establish new activity standards for ethylene polymerization. The system attains exceptional catalytic efficiencies (up to 10^8 g·mol$_{Ni}^{-1}$·h^{-1}), comparable to those of the most sophisticated group 4 metallocenes, while generating linear polyethylenes with adjustable molecular weights (M_n of about 2.5×10^5 g·mol^{-1}) in saturated alkane solvents, which is a vital attribute for industrial slurry-phase processes. An essential novelty is found in the hydroxyl-functionalized *α*-ketoimide version, in which pendant —OH groups participate in hydrogen bonding with SiO_2 supports. This non-covalent immobilization method produces resilient hetero phase catalysts that maintain over 90% activity at high temperatures (70–80 °C), while preventing reactor fouling by enhancing polymer morphology. This method bypasses conventional covalent grafting, maintains active site accessibility, and facilitates catalyst recycling, which is an important advancement for continuous-flow production. In addition to performance measurements, the modularity of the *α*-ketoimide scaffold enables systematic adjustment of the electronic and steric characteristics. Subsequent investigations[157,158] revealed that variations in substituents at the ligand periphery (*e.g.*, electron-donating alkyl versus. electron-withdrawing aryl groups) significantly influence the chain-walking behavior and comonomer insertion. For example, larger substituents inhibit *β*-hydride elimination, facilitating the production of ultrahigh-molecular-weight polyethylene (UHMWPE, $M_n>10^6$ g·mol^{-1}) under moderate circumstances. This study demonstrated that *α*-ketoimide ligands serve as diverse and synthetically attainable foundations for connecting homogeneous and heterogeneous catalysis. Chen's design concepts integrate atomic-level accuracy with industrial practicality, facilitating the advancement of next-generation polyolefin technologies, particularly in industries requiring high thermal stability and sustainable processes.

7 CONCLUSIONS

Nickel-based catalysts have transformed olefin polymerization, providing exceptional control over polymer structure and properties. Researchers have addressed the historical limitations in thermal stability and chain-transfer suppression through strategic ligand design, including steric bulk, electronic asymmetry, and cooperative dinuclear systems. This advancement has facilitated the synthesis of UHMWPEs, branched elastomers, and polar-functionalized copolymer materials. The chain-walking mechanism, which is a characteristic of *α*-diimine systems, has been utilized to develop materials with adjustable crystallinity and mechanical properties. Recent progress in aqueous-phase polymerization and photodegradable polyolefins corresponds to global sustainability objectives, addressing environmental is-

sues related to plastic waste. Challenges remain in attaining high-fidelity polar monomer incorporation and scaling lab-based innovations for industrial applications. Future efforts should emphasize ligand modularity, conduct mechanistic studies through computational modeling, and develop scalable green synthesis techniques. The increasing demand for high-performance and recyclable polymers makes nickel catalysts pivotal in advancing precision polyolefin chemistry, thereby presenting significant implications for materials science and circular economies.

BIOGRAPHIES

Muhammad Asadullah Khan obtained his M.S. degree from Anhui Agricultural University, China, in 2021 under the supervision of Prof. Zhen Chen. He then joined the research group of Prof. Changle Chen as a Ph.D. candidate, where he conducted research on catalyst development and polymerization chemistry, earning his Ph.D. degree in 2025. He is currently pursuing postdoctoral research at Anhui University under the supervision of Prof. Fuzhou Wang. His current research focuses on the development of advanced catalysts and innovative methodologies for olefin polymerization and copolymerization, with particular interests in catalyst design, polymer microstructure control, and sustainable polymer synthesis.

Obaid Iqbal received his M.S. degree in 2015 from University of the Punjab. He carried out his doctoral work in polymer processing engineering at University of Science and Technology of China under the direction of Prof. Liangbin Li from 2016 to 2021. Subsequently, he joined Prof. Fuzhou Wang group at Anhui University each year as a research assistant. In 2024, he joined Anhui University as a lecturer. His current research interest is focused on olefin polymerization, olefin processing and engineering.

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Fu-Zhou Wang received his Ph.D. degree from Hiroshima University under the direction of Prof. Takeshi Shiono from 2013 to 2017. Subsequently, he joined Prof. Changle Chen's group at the University of Science and Technology of China for 1 year as a research assistant. In 2018, he joined Anhui University as an associate professor and was promoted to full professor in 2025. He leads a polyolefin R&D team dedicated to the industrial development and application of high-performance polyolefin materials. Meanwhile, as the deputy director of the Chuzhou Research Institute of Anhui University, he also leads an entrepreneurial team committed to the development of vehicle systems utilizing new energy batteries/photovoltaic technologies, and high-polymer processing precision equipment.

Conflict of Interests

The authors declare no interest conflict.

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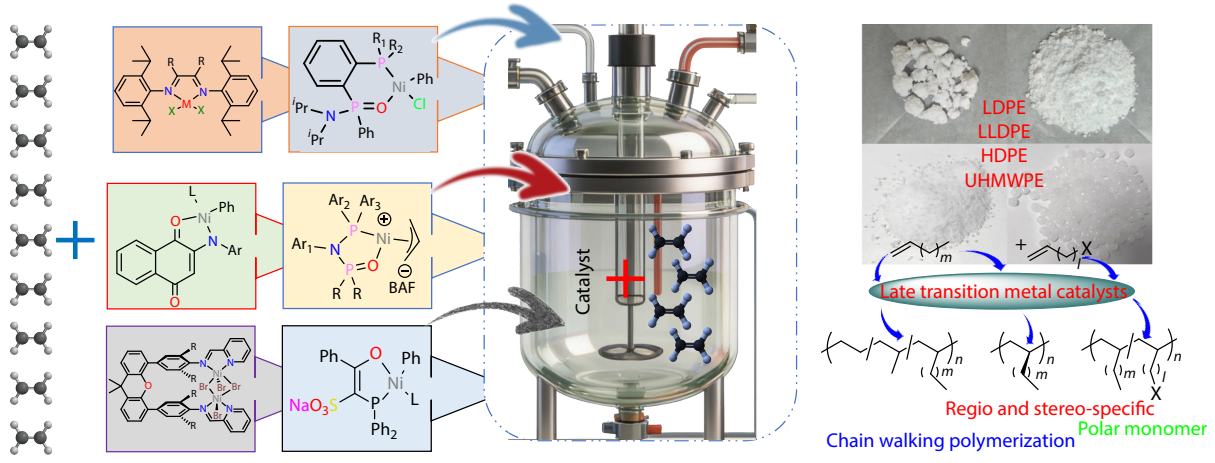
Graphical Abstract

Recent Advancements in Nickel-catalyzed Olefin Polymerization: Molecular Design, Mechanistic Insights, and Sustainable Polyolefin Materials

Muhammad Asadullah Khan, Obaid Iqbal, Zi-Hao Wang, and Fu-Zhou Wang

Anhui University; University of Science and Technology of China

A versatile platform of late transition metal catalysts has been developed for the precision polymerization of ethylene. By leveraging tunable ligand designs and controlled chain-walking mechanisms, these catalytic systems enable the tailored synthesis of diverse polyethylene architectures, ranging from highly branched LDPE to linear HDPE and UHMWPE. Furthermore, the catalysts demonstrate exceptional regio- and stereo-specificity, facilitating the direct copolymerization of ethylene with polar monomers to produce advanced, functionalized polyolefins.



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