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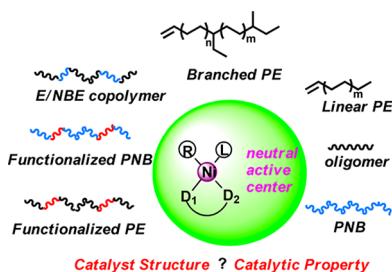
Neutral Nickel Catalysts for Olefin Homo- and Copolymerization: Relationships between Catalyst Structures and Catalytic Properties

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1. INTRODUCTION AND SCOPE OF REVIEW

As one milestone in the history of polymerization chemistry, the work of Ziegler and Natta has led to the rapid commercialization of transition metal catalysts for the production of high molecular weight polyolefins.^{1–4} However, the heterogeneous nature of Ziegler–Natta catalytic systems has hindered better understanding of the polymerization mechanisms, resulting in great difficulties in the design of new catalysts. The advance of homogeneous single-site metallocene catalysts together with the discovery of methylaluminoxane (MAO) is a real breakthrough in understanding the relationship between catalyst structure and catalytic behaviors in olefin polymerization. A more precise control over polymer microstructures has been achieved through modification of the metallocene catalytic systems,^{5–7} which greatly invigorates the development of new single-site catalysts (postmetallocene catalysts) based on both early and late transition metals.^{8–17}

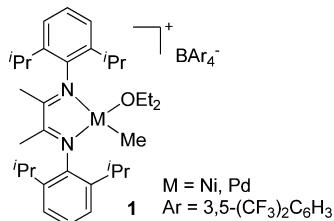
The highly electron-deficient early metal catalysts tend to be poisoned by polar functional groups. In contrast, late metal catalysts exhibit a great potential in the manufacture of valuable functionalized hydrocarbon polymers thanks to their much

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lower oxophilicity.^{18,19} In 1995, Brookhart et al. reported their seminal discovery on cationic Ni(II) and Pd(II) catalysts bearing bulky α -diimine ligands (e.g., 1, Chart 1),^{20–22} which

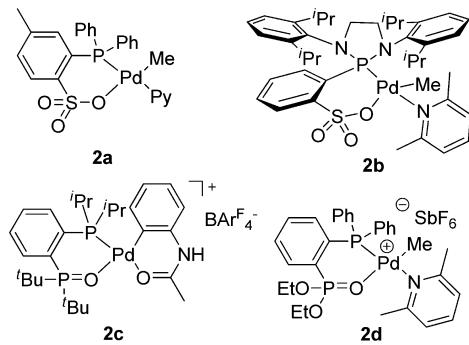
Chart 1. Examples of α -Diimine Catalysts Reported by Brookhart's Group



provide high molecular weight branched polyolefins, and even copolymerize α -olefins with commercially available polar monomers such as methyl acrylate. These findings have triggered significant research in this field, leading to the development of many efficient late metal catalysts.

With the notion that neutral catalysts may exhibit higher functional group tolerance, Pugh et al. have developed the renowned neutral palladium catalysts supported by phosphine–sulfonate ligands (e.g., complex 2a, Chart 2). The catalytic

Chart 2. Palladium Catalysts Capable of Copolymerizing Ethylene with Polar Monomers

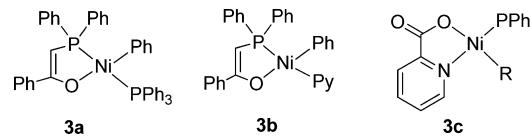


system was first used *in situ* in 2002 to give ethylene/MA linear copolymer,²³ and has since found great applications in the copolymerization of ethylene with various other polar monomers such as vinyl acetate (VA), acrylonitrile (AN), vinyl halide, vinyl ethers, carbon monoxide, and others. This work represents an unprecedented example of coordinative insertion copolymerization of ethylene with readily available polar monomers to produce linear copolymers, inspired by which new palladium catalysts based on other frameworks mimicking the structural features of phosphine–sulfonate ligands have also emerged (e.g., complex 2b–d).^{24–27} Nozaki et al. summarized the development of phosphine–sulfonate neutral palladium catalysts in 2009,¹⁹ 2013,²⁸ and very recently.²⁹ The authors displayed that four reactions can be realized by using this catalytic system: (1) the production of high molecular weight linear polyethylene (PE) using group 10 metal catalysts; (2) affording linear copolymers by copolymerization of olefin with polar monomers; (3) carbon monoxide/ethylene nonalternating copolymerization; and (4) copolymerization of common polar monomers with monoxide.

Despite these developments of phosphine–sulfonate and α -diimine palladium catalysts, there have been imperious needs

for the discovery of inexpensive and generally more active nickel catalysts. Shell Higher Olefin Process (SHOP) neutral nickel catalysts (e.g., Chart 3) discovered by Keim et al. have

Chart 3. Typical SHOP Catalysts for the Production of Linear α -Olefins



been successfully commercialized for the preparation of α -olefins.³⁰ These catalysts are also capable of copolymerizing ethylene with some comonomers bearing functional groups remote from the olefinic double bond.^{31,32} Since then, no significant progress has been made in neutral nickel catalysts until the end of the 20th century when Grubbs et al.^{33,34} and Johnson et al.³⁵ reported a series of neutral nickel catalysts to give high molecular weight polymers and show substantial tolerance toward polar agents. These investigations have aroused renewed interest in neutral nickel catalysts for olefin polymerization, and large arrays of effective catalysts have been developed in the following years. While the catalysts supported by various ligand frameworks may exhibit distinct catalytic behaviors in olefin polymerization, most of them have common features of good functional group tolerance, facile initiation, and the possibility of chain walking. These unique features make neutral nickel catalysts an attractive choice for olefin polymerization.

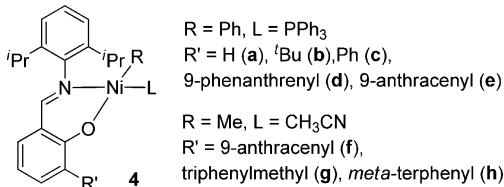
This Review describes the main advances in olefin homo- and copolymerization using neutral nickel catalysts in recent years. Complexes containing Ru^{36–40} and Rh^{41–43} have rarely been used in olefin polymerization, and Fe, Co catalysts⁴⁴ are mostly related to a mechanism with cationic active sites. These catalysts and the aforementioned palladium systems that have been extensively reviewed by Nozaki et al.^{19,28,29} are therefore not included in this Review. In view of the perspective presented by Matt et al.,³² most of the SHOP-type catalysts for ethylene oligomerization and polymerization are also not included. Although neutral nickel catalysts have been partly summarized in previous articles,^{16,19,45–51} our effort is to present a comprehensive review on the development in this field. Herein, we summarize the literature according to the types of catalysts, focusing on the relationship between catalyst structure and catalytic performance. In this Review, catalytic activities have been converted, where necessary, into the unit of g/mol_{cat}·h.

2. PHENOXY–IMINE NICKEL COMPLEXES

2.1. Ethylene Polymerization

Salicylaldimine complexes of group 4,^{52–54} group 5,^{55–57} and group 6⁵⁸ transition metals for olefin polymerization have been well investigated and are of great importance to polymer synthesis. In 1998, Grubbs et al. reported the first array of salicylaldiminato nickel complexes that are active for ethylene polymerization with the aid of Ni(COD)₂ or B(C₆F₅)₃.³³ A bulky group at the ortho position of the phenoxy moiety is found to enhance the catalytic activity and molecular weight of the resulting PE. Subsequently, complexes 4c–e (Chart 4) were described to be highly active catalysts for ethylene polymerization in the absence of any cocatalyst.³⁴ In particular,

Chart 4. Salicylaldiminato Neutral Nickel Catalysts Developed by Grubbs' Group



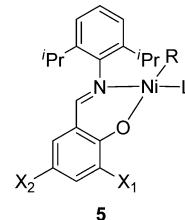
complex **4e** bearing a bulky 9-anthracyenyl group exhibits a catalytic activity (up to 3.7×10^6 g PE/mol_{Ni}·h) much higher than that of the parent complex **4a** (1.6×10^5 g PE/mol_{Ni}·h). This value is comparable to those of classical metallocene catalysts such as $(Cp_2ZrMe)^+[B(C_6F_5)_4]^-$ (4.5×10^6 g PE/mol_{Zr}·h), and the cationic nickel catalysts developed by Brookhart et al.^{20–22} High molecular weight ($M_w > 2.50 \times 10^5$) PEs with fewer than 10 branches per 1000 carbons are obtained using these neutral nickel catalysts. More importantly, these catalysts are able to polymerize ethylene in the presence of functional additives such as ethers, esters, alcohols, amines, and water, and incorporate polar monomers into the polymer backbone in variable quantities.³⁴ The bulky group ortho to the phenoxy moiety is found to accelerate PPh₃ dissociation and decrease the rate of catalyst deactivation, which is considered to be crucial for the high performance of these catalysts.

In the wake of Grubbs' report on efficient catalysts **4a–h**, extensive investigations on neutral nickel catalysts have been conducted. Research has mainly focused on salicylaldimine frameworks thanks to their amenability to structural modifications.¹⁶ These novel catalysts have been used in olefin polymerization and copolymerization under various conditions. Studies have been carried out on the functions of the additional stabilizing ligands and the electronic/steric effects of substituents.

2.1.1. Effect of C-3 and C-5 Substituents. Bulky groups ortho to the phenoxy moiety (C-3 position) are very important for neutral nickel catalysts due to their ability to prevent the formation of bis-ligated complexes and accelerate the dissociation of pendant phosphine ligands. Many investigations have emerged in related systems after Grubbs' contribution (e.g., complex **5a–m**, Table 1). Electronic effects of the substituents para to the phenoxy moiety have also been reported to significantly influence the polymerization (e.g., **5b–d**),^{59,60} whereas little is known about the function of ortho electronic effects on catalytic performance. Li et al. therefore investigated neutral nickel catalysts **5f–5k** with ligands bearing various ortho-substituted aryl groups (Table 1).⁶¹ Electron-withdrawing substituents, such as nitro (**5g**) and pentafluorophenyl groups (**5h–k**), lead to high catalytic activity comparable to that of Grubbs' catalyst **4e**. Polymers with slightly lower molecular weight are obtained, possibly due to the accelerated chain-transfer rate caused by the electron-withdrawing groups. The nonphosphine additional stabilizing ligands, such as pyridine (**5i**) and the $\eta^3\text{-CH}_2\text{Ph}$ ligand (**5k**), are found to be beneficial for polymerization initiation, albeit at the expense of catalyst lifetime to some extent.

C-3 substituents in phenoxy-imine frameworks are situated in close proximity to the nickel center and thus tend to exercise significant influences on polymerization characteristics. In this regard, intramolecular hydrogen bonding of neutral nickel catalyst has been reported to greatly affect the catalytic performance by Li et al.⁶⁵ and Marks et al.⁶⁶ Complexes **6a**

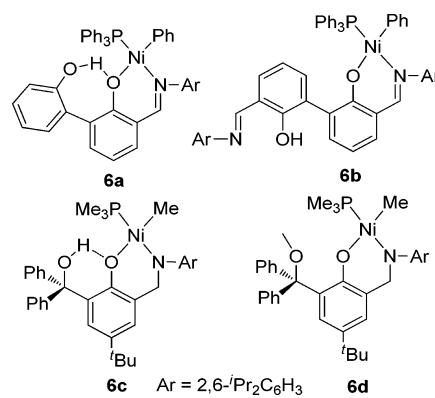
Table 1. Neutral Nickel Ethylene Polymerization Catalysts with Different C-3 and C-5 Substituents



complex	X ₁	X ₂	R	L	ref
5a	C ₆ H ₁₁	H	Ph	PPh ₃	62
5b	OMe	Cl	Me	Py	59
5c	OMe	Br	Me	Py	59
5d	I	I	Me	Py	59, 60
5e	9-anthracyenyl	H	Me	Py	63
5f	2'-OMeC ₆ H ₄	H	Ph	PPh ₃	61
5g	2-NO ₂ C ₆ H ₄	H	Ph	PPh ₃	61
5h	C ₆ F ₅	H	Ph	PPh ₃	61
5i	C ₆ F ₅	H	Me	Py	61
5j	C ₆ F ₅	H	PM ₃	$\eta^1\text{-CH}_2\text{Ph}$	61
5k	C ₆ F ₅	H	$\eta^3\text{-CH}_2\text{Ph}$		61
5l	'Bu	H	Me	PM ₃	64
5m	CF ₃	H	Me	PM ₃	64

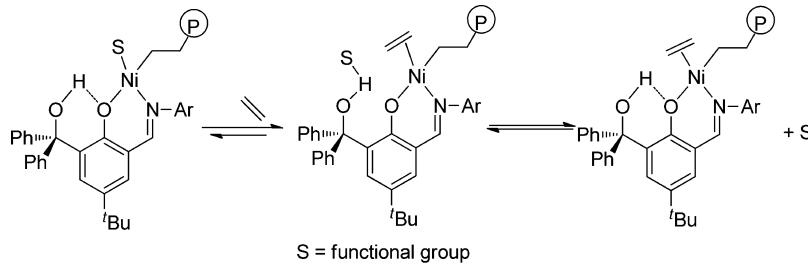
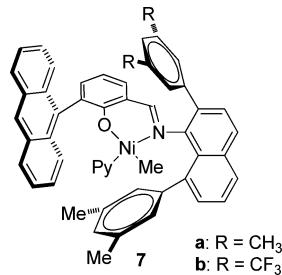
and **6b** exhibit high catalytic activities up to 11.4 and 14.7×10^5 g PE/mol_{Ni}·h, respectively, much more active than **4c** without a free hydroxyl group (1.0×10^5 g PE/mol_{Ni}·h under slightly different conditions).⁶⁵ The branching content of the polymers produced by **6** (especially **6a**) is notably higher than that by **4c** (Table 2), whereas the molecular weight shows an opposite trend. This indicates a more prominent chain walking for **6a** and **6b**. These complexes can be covalently bonded to the

Table 2. Effects of Hydrogen Bonds in Salicylaldiminato Ni Catalysts on Ethylene Polymerization^a



complex	activity (10^5 g PE/mol _{Ni} ·h)	M_w^d ($\times 10^3$)	D_M^d	branches/1000C
6a	11.4	6.5	3.2	90
6b	14.7	72.6	3.2	25
4c^b	1.0	207.0	2.2	10
6c^c	11.8	6.7	1.8	60
6d^c	4.7	7.4	2.0	44

^aPolymerization conditions: toluene, 60 mL; complex, 10 μmol ; ethylene, 2.1 MPa; 40 °C; 60 min. ^bToluene, 90 mL; complex, 65 μmol ; ethylene, 0.7 MPa; 10 °C external bath. ^cToluene, 25 mL; complex, 10 μmol ; 2 equiv of Ni(COD)₂; ethylene, 0.8 MPa; 25 °C; 40 min. ^dDetermined by GPC.

Scheme 1. Influence of Hydrogen Bond on the Interaction of Polar Additives with a Nickel Center**Table 3. Neutral Nickel Catalysts with 2,8-Diarylnaphthalyl-Substituted N-Aryl Groups^a**

complex	ethylene (MPa)	time (min)	activity (10^5 g PE/mol _{Ni} ·h)	M_n ($\times 10^3$)	D_M	branches ^c /1000C
7a	1.4	30	13.2	550	2.8	28
7a	2.8	30	23.2	1008	2.8	20
7b	1.7	30	17.4	865	2.5	9
7b	2.8	30	31.1	1096	2.4	7
7a ^b	0.7	20	9.8	491	1.38	— ^d
7a ^b	0.7	30	9.0	777	1.31	— ^d
7a ^b	0.7	60	8.4	1228	1.47	— ^d
7a ^b	0.7	120	9.8	160	2.11	— ^d

^aPolymerization conditions: toluene, 200 mL; complex, 5 μmol ; 50 °C. ^b10 equiv of Ni(COD)₂ was used; 28 °C. ^cDetermined by ¹H NMR. ^dNot determined.

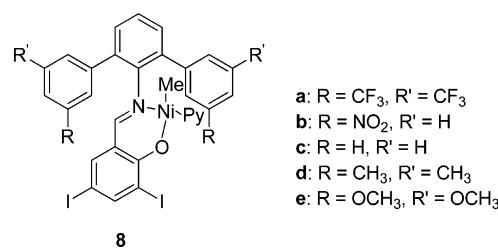
support by reacting with activated silica, and the two immobilized catalysts produce PE with higher M_w ($>1.2 \times 10^5$). Likewise, hydrogen-bonded catalyst 6c (Table 2) is 2.5 times more active than the non-hydrogen-bonded 6d and gives PE with a much higher degree of branching.⁶⁶ Moreover, better tolerance toward polar additives (such as ether, acetone, and water) for the hydrogen-bonded 6c is also observed in ethylene polymerization. The intramolecular hydrogen bond directed toward the active site is supposed to accelerate β -hydrogen elimination/reinsertion processes. An interaction between the functional group and the free hydroxyl group is thought to protect the active species from deactivation (Scheme 1).⁶⁶ Further detailed investigations, however, are needed to support these assumptions.

2.1.2. Effect of N-Aryl Imine Moieties. Neutral nickel catalysts with less bulky N-aryl imine moieties are not effective for ethylene polymerization, probably due to the failure to block the axial position at the metal center. To overcome this, Daugulis and Brookhart et al. designed neutral nickel catalysts 7a and 7b bearing a 2,8-diarylnaphthalyl-substituted N-aryl group (Table 3).⁶⁷ These bulky groups effectively shield the axial sites and retard chain transfers, leading to the production of moderately branched ultrahigh-molecular-weight polyethylene (UHMWPE, M_n up to 1.6×10^6). This is unique considering that previously reported UHMWPEs are mostly linear^{68–74} or extremely highly branched ones.⁷⁵ Moreover, molecular weights of the polymers produced by the $-\text{CH}_3$ substituted complex 7a (with the activation of Ni(COD)₂) increase linearly with

reaction time, which is a characteristic of living polymerization, although the molecular-weight dispersities (D_M) are greater than expected for a living process. This phenomenon is similar to that observed by Bazan et al. using α -imino carboxamidato nickel catalysts (vide infra, section 3.1.1).⁴⁷

Modifications on the terphenyl N-aryl moiety of the salicylaldiminato backbone have been systematically investigated by Mecking et al. to examine the relationships between ligand structures and catalytic behavior.⁷⁶ A series of surprising and unprecedented effects of remote substituents on polymer branching and molecular weight have been disclosed.

Both the molecular weights and the branching degrees of the polymers have a strong dependence on the electron-withdrawing character ($8e \approx 8d < 8c < 8b \approx 8a$, Chart 5) of the substituents in catalysts 8a–e, whereas the same trend does not

Chart 5. Salicylaldiminato Ni(II)–Me Pyridine Catalysts Developed by Mecking et al.

exist for the catalytic activities (Figure 1). Higher molecular weight polymers are readily obtained using more electron-

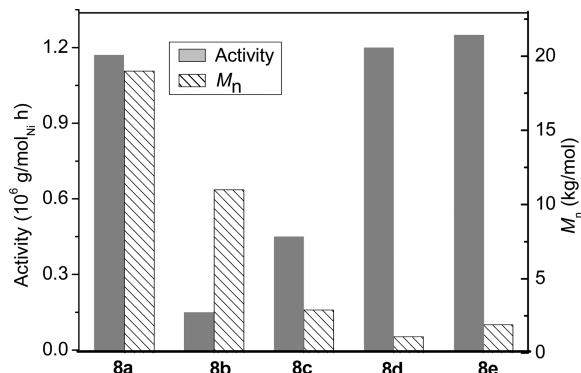


Figure 1. Catalytic activities and M_n 's of the PEs produced by 8a–e. Conditions: toluene, 100 mL; ethylene, 4.0 MPa; 50 °C; 0.5 h.

deficient catalysts, possibly due to the restraints of chain transfer by the electron-withdrawing groups, despite their remoteness from the metal center.⁷⁶ Interestingly, catalyst 8d that produces the lowest molecular weight branched polymer has been utilized to synthesize monofunctionalized hyperbranched ethylene oligomers, which are potentially useful as lubricants or surface modifiers.⁷⁷

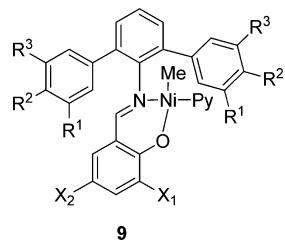
More thorough investigations have also been conducted by Mecking et al. (Table 4)^{63,78} on the substituent effects of the terphenyl moieties in salicylaldiminato Ni(II)–Me catalysts (including the aforementioned 8a,b,e). Complexes 8a,b,e and 9a–m are highly active, single-component catalysts for ethylene polymerization, affording PEs with a wide range of microstructures. Electron-withdrawing as well as sterically demanding

3',5'-substituents of the terphenyl group reduce the branching degree of the resultant PEs but increase the molecular weight, which is consistent with the previous results.⁷⁶ Moreover, variation of the substituent ortho to the phenoxy group has a major impact on the catalytic activity toward ethylene polymerization. Diiodo-substituted complex 8a and anthracenyl-substituted 9d show comparable activities (1.1×10^6 vs $1.2 \times 10^6 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$), which are much higher than those of 9k ($3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$) and 9m ($3-\text{t-Bu}$) (2.7×10^5 and $0.1 \times 10^5 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$).⁶³ Catalysts 8a,b,e and 9a–m with bulky terphenyl groups produce PEs with lower molecular weight ($M_n < 4.3 \times 10^4$) than the classical catalyst 5e ($M_n = 2 \times 10^5$) under similar reaction conditions. Also noteworthy is that the complexes bearing 3,5-CF₃-substituted N-aryl groups (e.g., 9k–m) are much more stable than the other terphenyl analogues (including the anthracenyl-substituted 9e–j). This implies a possibly different decomposition mechanism for terphenyl systems from that of conventional diisopropyl-substituted ones.

Apart from complexes 8 and 9 that have 2,6-di(3,5-(R)₂-phenyl)phenyl moieties in the ligands, 10a–h bearing 2,6-di(4-R-phenyl)phenyl groups have also been designed to differentiate the influence of electronic and steric effects on catalytic polymerization.⁷⁸ After examining the ethylene polymerization results (Table 5), the electronic and steric effects of the substituents, and the solid-state structure of complex 10c, the authors concluded that the polymer molecular weight and degree of branching are controlled exclusively by electronic rather than steric effects of the substituted R group.

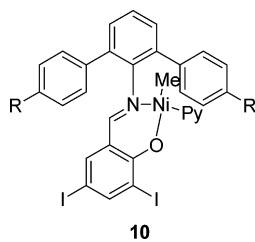
Marks et al. demonstrated that PEs with distinct molecular weight and branch content can be obtained using catalysts 11a and 11b that have only minor differences in their structures (Table 6). The non-negligible C_β–H_β···F₃C dipolar interactions in 11b are proposed to be responsible for the less favorable β-H elimination during polymerization, resulting in the production

Table 4. Salicylaldiminato Ni(II)–Me Pyridine Catalysts with Bulky Imine Moieties^a



complex	X ₁	X ₂	R ¹	R ²	R ³	activity ^c	$M_w (\times 10^3)$	D_M
5e	9-anthracenyl	H				12.9	400.0	2.0
9a	I	I	tBu	H	tBu	15.1	29.7	2.7
9b	I	I	tBu	OH	tBu	14.8	28.0	2.0
9c	I	I	Me	OMe	Me	7.28	1.68	2.1
9d	9-anthracenyl	H	CF ₃	H	CF ₃	12.0	129.0	3.0
9e	9-anthracenyl	H	tBu	H	tBu	19.9	30.8	2.8
9f	9-anthracenyl	H	tBu	OH	tBu	12.6	44.8	2.8
9g	9-anthracenyl	H	Me	H	Me	13.7	12.5	3.9
9h	9-anthracenyl	H	Me	OMe	Me	7.6	2.4	2.7
9i	9-anthracenyl	H	OMe	H	OMe	5.3	17.2	4.3
9j	9-anthracenyl	H	OMe	OMe	OMe	6.4	53.0	5.3
9k ^b	$3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$	$3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$	CF ₃	H	CF ₃	2.7	46.0	2.3
9l ^b	H	NO ₂	CF ₃	H	CF ₃	7.5	20.4	2.4
9m ^b	tBu	H	CF ₃	H	CF ₃	1.0	21.1	2.2

^aPolymerization conditions: toluene, 100 mL; complex, 10 μmol; ethylene, 4.0 MPa ; 50 °C; 40 min. ^bToluene, 200 mL; complex, 40 μmol (9k), 20 μmol (9l), 15 μmol (9m); 60 min. ^cIn the unit of $10^5 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$.

Table 5. Polymer Structure Control by Electronic Effects of Remote Substituents^a

complex	R	σ_p^d	branches/ 1000C	activity ^e	M_n^e ($\times 10^3$)	D_M
10a ^b	C ₈ F ₁₇	0.48	23	13.7	3.5	2.2
10b ^c	CF ₃	0.54	30	23.4	4.2	2.1
10c ^c	F	0.06	37	9.5	3.0	2.2
10d	H	0	52	22.4	2.9	2.3
10e	Me	-0.17	56	6.4	1.0	2.3
10f ^b	tBu	-0.20	70	11.5	0.8	2.1
10g	OMe	-0.27	64	5.3	0.9	2.4
10h ^b	NMe ₂	-0.83	102	2.2	0.7	2.3

^aPolymerization conditions: toluene, 100 mL; complex, 40 μ mol; ethylene, 4.0 MPa; 50 °C; 1 h. ^bComplex, 20 μ mol. ^c2 h. ^dHammett constants. ^eIn the unit of 10^4 g PE/mol_{Ni}·h.

of higher molecular weight PE (**11b**, $M_w = 9.2 \times 10^4$ vs **11a**, $M_w = 1.4 \times 10^3$).⁷⁹ However, Mecking et al. designed a similar catalyst **11c** with four electron-withdrawing nitro substituents, and found that this catalyst produces even higher molecular weight polymers than the corresponding $-CF_3$ analogue **8a** (vide supra). These results indicate that $-CF_3$ groups in this family of catalysts are not singular in depressing chain-transfer reactions, which could also be achieved by electron-withdrawing substituents.⁸⁰

In 2014, there came another example concerning the modification of N-aryl groups of phenoxy-imine neutral nickel catalysts, which supports that minor alteration in steric bulk can lead to striking differences in catalytic behavior.⁸¹ Marks et al. found that the spatially proximate but electronically remote weakly coordinating $-SO_2-$ moiety significantly enhances the catalytic activity and thermal stability. This catalyst produces PE with more branches and higher molecular weight than the analogous complex bearing the $-CH_2-$ moiety (Table 7, **12b**, 98 branches/1000 carbon atoms, $M_w = 1100$; **12a**, 148

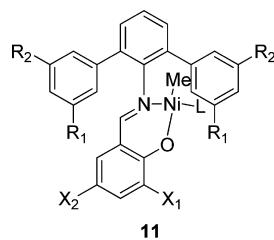
branches/1000 carbon atoms, $M_w = 3500$).⁸¹ The authors ascribed this difference to the more facile β -H elimination/olefin reinsertion process. Moreover, DFT analysis indicates that the nickel center is greatly stabilized by the proximate $-SO_2-$ group.

Catalysts containing olefin functional groups affiliated to the ligand can be used as comonomers during polymerization, permitting the self-immobilization of the catalysts to the resultant polymer. Alt et al. developed metallocene catalysts that immobilized in the polymerizations of ethylene and propylene.^{5,82} Subsequently, Jin et al. synthesized a series of neutral, single-component salicylaldiminato nickel catalysts bearing allyl substituents as self-immobilized catalysts that produce linear polymers.^{83,84} The steric bulk of R^2 or R^3 substituents greatly influences the catalytic activity because of their shield of the axial faces and suppression of chain termination reactions (Table 8). For example, complex **13d** displays a catalytic activity of 1.8×10^5 g PE/mol_{Ni}·h, whereas **13a** and **13c** are inactive for ethylene polymerization.⁸³ A dramatic increase in catalytic activity is observed due to the self-immobilization, with **13d** much more active than allyl-free **4c**.⁸⁴ Interestingly, the self-immobilized neutral nickel catalysts are tolerant of polar monomers (e.g., MA) added to the catalytic systems.

A proposed mechanism for the self-immobilization process of the catalysts is illustrated in Scheme 2.⁸³ In the polymerization process, the copolymerization of ethylene and the pendant allyls makes the catalyst molecules immobilize on polymer chains. Consequently, the homogeneous catalyst is transferred to a heterogeneous system without requiring any support, giving rise to PEs with unique microstructures.⁸⁴

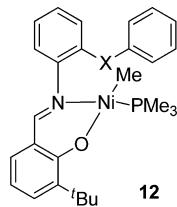
2.2. Norbornene Polymerization

The coordinative insertion polymerization of norbornene (NBE) yields 2,3-connected, rotationally constrained vinyl-type polynorbornenes (PNBs) bearing unique physical properties, such as good chemical and UV resistance, low dielectric constant, high glass transition temperature (T_g), excellent transparency, high refractive index, and low birefringence.^{46,85–88} In the presence of neutral nickel catalysts, high molecular weight vinyl-type PNBs have been prepared.⁴⁶ Salicylaldiminato complexes **4a–c** and **14a–e** (Table 9) are highly active toward NBE polymerization upon the activation of modified methylaluminoxane (MMAO).⁸⁹ The maximum

Table 6. Chain-Transfer Depressing Using Catalysts Bearing Electron-Withdrawing Groups^a

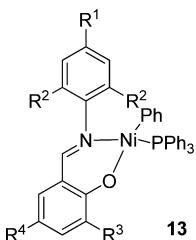
complex	L	X ₁	X ₂	R ¹	R ²	activity ^c	M_w ($\times 10^3$)	D_M
11a	PM ₃	tBu	H	CH ₃	CH ₃	3.0	1.4	1.1
11b	PM ₃	tBu	H	CF ₃	CF ₃	20.0	92.0	3.0
11c ^b	Py	I	I	NO ₂	NO ₂	2.4	152.6	3.2
8a ^b	Py	I	I	CF ₃	CF ₃	21.2	126.4	4.0

^aPolymerization conditions: toluene, 50 mL; complex, 5 μ mol; ethylene, 0.8 MPa; 23 °C; 10 min. ^bToluene, 100 mL; complex, 10 μ mol; ethylene, 4.0 MPa; 50 °C; 40 min. ^cIn the unit of 10^5 g PE/mol_{Ni}·h.

Table 7. Neutral Nickel Catalysts Bearing $-\text{SO}_2-$ and $-\text{CH}_2-$ Ligands^a

complex	X	activity (10^5 g PE/mol _{Ni} ·h)	branches ^b /1000C	$M_w (\times 10^3)$	D_M
12a	SO_2	2.85	148	3.5	1.8
12b	CH_2	0.18	98	1.1	1.4

^aPolymerization conditions: toluene, 25 mL; complex, 10 μmol ; $\text{Ni}(\text{cod})_2$, 20 μmol ; ethylene, 0.8 MPa; 23 °C; 40 min. ^bBy ^1H NMR.

Table 8. Self-Immobilized Nickel Catalysts Bearing Allyl Substituent at the Imine Moiety^a

complex	R ¹	R ²	R ³	R ⁴	activity ^b	$M_w (\times 10^3)$	D_M
13a	allyl	ⁱ Pr	H	H	0	— ^c	— ^c
13b	allyl	ⁱ Pr	NO_2	NO_2	2.9	192.4	32.0
13c	allyl	ⁱ Pr	^t Bu	Me	0	— ^c	— ^c
13d	allyl	ⁱ Pr	Ph	H	1.8	66.4	12.8
13e	allyl	Me	Ph	H	0.9	121.8	4.6
4c	H	ⁱ Pr	Ph	H	0.1	207.0	2.2

^aReaction conditions: toluene, 120 mL; complex, 65.4 μmol ; ethylene, 0.4 MPa; 27 °C; 1 h. ^bIn the unit of 10^5 g PE/mol_{Ni}·h. ^cNot determined.

catalytic activity of 7.08×10^7 g PNB/mol_{Ni}·h is achieved in low monomer concentration in feed (1.3 mol/L), and high molecular weight (1.5×10^6) PNB with high T_g (>400 °C) is obtained. Interestingly, steric effects of various substituents at the catalyst backbone show only negligible influence on the polymer yields and molecular weights, which is clearly different from the observations in ethylene polymerization catalyzed by neutral nickel catalysts.

14f–k/MAO (Table 9, R⁴ = 1-naphthyl) catalytic systems reported by Sun's group can promote the vinyl polymerization of NBE with an activity up to 2.86×10^8 g PNB/mol_{Ni}·h.⁹⁰ The complexes with more electron-withdrawing chloro substituents

on the ligands are more active than those with iodo substituents. Steric effects of the more bulky iodo atoms may also have played a negative role in NBE polymerization. Further modification of the ligand structure was conducted by Jin's group (15a,b).⁹¹ Catalytic activity as high as 3.35×10^7 g PNB/mol_{Ni}·h is achieved by the 15a/MMAO catalytic system, producing high molecular weight ($M_w > 10^6$) PNB (Table 10). Catalyst 15b bearing isopropyl groups at the R positions is less active than the analogue 15a bearing methyl groups, which is again in contrast with the observations for ethylene polymerizations.

Catalysts 16a–d display higher (roughly doubled) activities than does 16e in NBE polymerization, and the difference in N-aryl group is supposed to be responsible for this result.⁹² Similar to previous reports, polymers with high molecular weight ($M_v > 10^6$) are obtained by use of these catalysts. Complexes 17a–i are synthesized and characterized for the addition polymerization of NBE in the presence of MMAO, and show high activities beyond 10^7 g PNB/mol_{Ni}·h (Table 11). Moreover, the fluorinated 17a–i are more active than the parent catalyst 16e under the same conditions.⁹³

2.3. Catalytic Copolymerization

It is desirable to expand the scope of PE applications through improving toughness, adhesion, gas diffusion characteristics, and miscibility with polar materials. These can be realized via copolymerization of ethylene with various comonomers such as α -olefins, cyclic olefins, and polar monomers. In particular, the introduction of functional groups into the backbone of PE has become more hopeful with the advent of late metal catalysts.³⁴ Grubbs et al. investigated the copolymerization of ethylene with polar monomers containing esters, alcohols, anhydrides, and amides using nickel catalysts and obtained linear functionalized PE in a single step (Scheme 3).⁹⁴

Scheme 2. Self-Immobilization of Neutral Nickel Catalysts

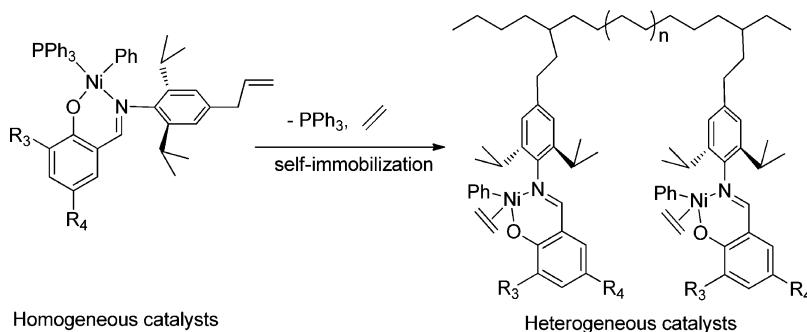
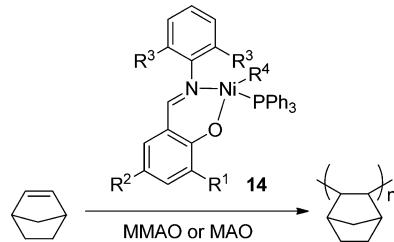
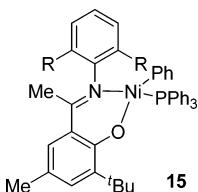


Table 9. Neutral Nickel Catalysts for NBE Polymerization via Addition Polymerization^a

complex	R ¹	R ²	R ³	R ⁴	yield (%)	activity ^b	M _v ^c ($\times 10^3$)	D _M
4a	H	H	iPr	Ph	87.8	330	1310	
4b	tBu	H	iPr	Ph	91.5	344	1310	
4c	Ph	H	iPr	Ph	87.8	330	1050	
14a	H	H	Me	Ph	33.5	126	1220	
14b	tBu	H	Me	Ph	83.5	314	1220	
14c	Ph	H	Me	Ph	85.6	322	1050	
14d	tBu	iBu	iPr	Ph	90.0	338	1140	
14e	tBu	tBu	Me	Ph	87.8	330	1220	
14f	I	I	iPr	1-naphthyl	78	2652	1954	4.5
14g	Cl	Cl	iPr	1-naphthyl	81	2715	711	6.9
14h	I	I	Et	1-naphthyl	80	2713	545	5.1
14i	Cl	Cl	Et	1-naphthyl	85	2866	951	9.1
14j	I	I	Me	1-naphthyl	75	2537	501	6.9
14k	Cl	Cl	Me	1-naphthyl	79	2671	747	8.8

^aPolymerization conditions: chlorobenzene, 15 mL; complex, 0.2 μ mol; Ni/Al/NBE = 1/2000/100 000; 30 °C; 15 min. Polymerization conditions (14f–k): toluene, 20 mL; catalyst, 5 μ mol; Ni/Al/NBE = 1/2000/20 000; 25 °C; 20 s. ^bIn the unit of 10⁵ g PNB/mol_{Ni}·h. ^cM_w for 14f–k, M_v for the others.

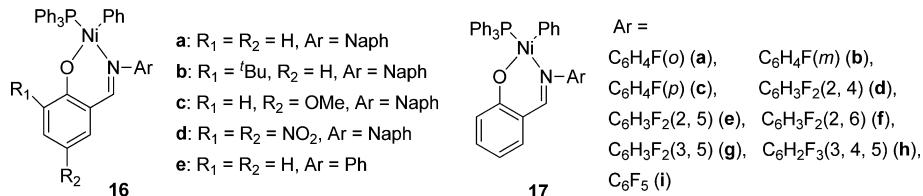
Table 10. Neutral Nickel Catalysts Bearing Schiff-Base Ligands for NBE Polymerization^a

complex	R	activity (10 ⁵ g PNB/mol _{Ni} ·h)	M _w ($\times 10^3$)	D _M
15a	Me	335	1356	2.5
15b	iPr	275	1142	2.4

^aPolymerization conditions: chlorobenzene, 10 mL; complex, 0.20 μ mol; MMAO as cocatalyst, Ni/Al/NBE = 1/11 000/136 000; 10 min.

2.3.1. Copolymerization with Nonpolar Monomer.

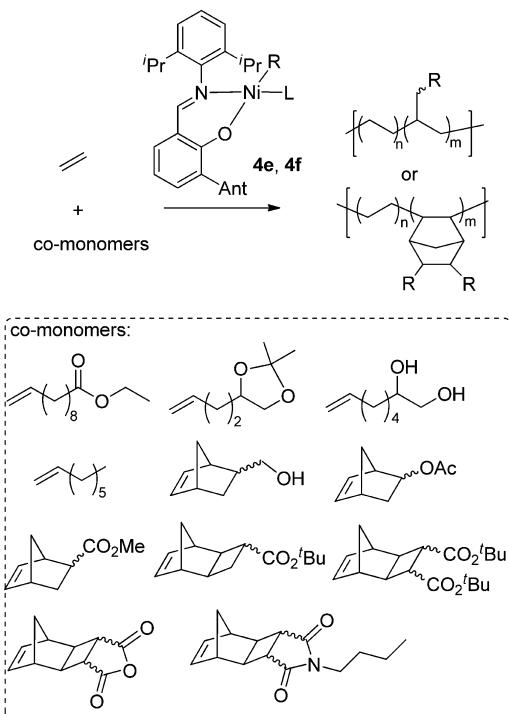
Highly active ethylene polymerization catalysts 4e and 4f³⁴ have been employed to copolymerize ethylene with 1-octene.⁹⁴ Low molecular weight copolymers (M_w = (3.3–12.8) $\times 10^3$) are obtained with moderate activities (10⁵ g polymer/mol_{Ni}·h), and the comonomer incorporation (1.7–12.5 mol %) can be modulated by varying reaction conditions. Copolymerization of ethylene with 1-butene is studied both in toluene and in water emulsion using nickel salicylaldiminato catalysts 5d, 8a, 8d, and 9q.⁹⁵ The catalytic activity is lowered by the difficult insertion of bulky 1-butene comonomer, and further decreases due to the slow insertion of the next monomer into the steric demanding Ni–alkyl species thus formed. Catalyst 8d, which has been known to have a stronger propensity for chain walking in ethylene homopolymerization, is much more active than 8a, 9q,

Table 11. NBE Polymerization by Nickel Complexes Bearing N-Naphthyl Salicylaldimine Ligands^a

complex	yield (%)	activity (10 ⁷ g PNB/mol _{Ni} ·h)	M _n ($\times 10^3$)	D _M
16a	60.38	3.41	777	3.2
16b	65.06	3.68	1070	2.7
16c	56.35	3.18	1070	2.8
16d	67.50	3.81	598	3.8
16e	29.63	1.67	771	3.1

^aPolymerization conditions: chlorobenzene, 15 mL; catalyst, 0.2 μ mol; MAO as the cocatalyst, Ni/Al/NB = 1/2665/100 000; 30 °C; 10 min.

Scheme 3. Copolymerization of Ethylene with Polar Monomers Using 4e and 4f



and **5d** (Table 12). It is proposed that the nickel center in catalyst **8d** could have “chain-walked” to form a less bulky Ni–alkyl species before the next insertion occurs.⁷⁶ For these different catalysts, ethylene insertion strongly dominates in the copolymerization resulting in low incorporation rates of 1-butene (<4.3 mol %), which is consistent with the result of ethylene/1-octene copolymerization reported by Grubbs et al.⁹⁴ ¹³C NMR data of the copolymers reveal that 1-butene is incorporated in 1,2-, 1,3-, and to a small extent 1,4-fashions.

Catalysts **8a**, **8d**, **9q**, and **5d** are also employed in ethylene/NBE copolymerization to modify the polymer crystallinity.^{60,95} Substitution patterns of the catalyst only slightly influence the NBE incorporations. Copolymers from amorphous to 65% crystallized can be obtained depending on the polymerization conditions, and the NBE incorporations range from 0.04 to 8.6 mol %.⁹⁵

2.3.2. Copolymerization with Polar Monomers. Introduction of polar functional groups into polyolefin materials

can lead to drastic changes in their physical and chemical properties. Currently, some polar monomers can be introduced into polyolefin via radical polymerization or other methods that allow little control over the polymer structure and comonomer composition.⁶⁷ In this respect, homogeneous single-site catalysts are strongly demanded considering their ability to copolymerize polar monomers with nonpolar olefins in a controlled manner. Late transition metals, especially neutral palladium catalysts, have been playing an important role in this field in the past decade.^{18,19} These catalysts successfully initiate the coordination–insertion copolymerization of ethylene with polar vinyl monomers, such as methyl acrylate (MA), vinyl acetate (VA), acrylonitrile (AN), vinyl halides, and vinyl ethers.¹⁹ Although some accomplishments have been achieved using a variety of transition metal complexes, the direct copolymerization of the aforementioned polar monomers with olefins remains a big challenge.

Several decades ago, SHOP catalysts were found to be capable of copolymerizing ethylene with polar monomers bearing functional groups remote from the olefinic double bonds.^{96,97} Besides, functionalized norbornenes could also be incorporated into PE materials at various rates using SHOP catalysts.⁹⁸ High incorporation up to 19 mol % is detected when the norbornene bearing ester group is used as the comonomer, albeit much lower than the value for ethylene/NBE copolymerizations (almost 50 mol %). However, SHOP catalysts completely fail to copolymerize the commercially available and less expensive vinyl polar monomers that have the olefinic double bonds directly connecting with the functional groups.

Recently, the catalyst efficiency and the comonomer incorporation have been greatly improved by rational design of bimetallic neutral nickel catalysts. The so-called cooperative effects between two metal centers are considered key for the enhanced catalytic performances.⁴⁹ Reports in connection with the copolymerization of olefins with polar monomers using binuclear catalysts will be detailed later (vide infra, section 5).

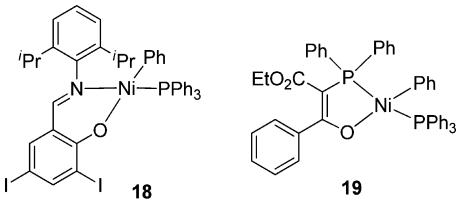
All of the examples mentioned above concerning polar monomer incorporation are based on a coordination–insertion mechanism, which has been generally considered as the major pathway for neutral nickel-catalyzed (co)polymerizations. However, it is also important to realize the possibility of metal-mediated radical processes, especially when polar monomers are used in the polymerizations.^{99,100} In 2011, Monteil et al. reported that **18** and **19** (Chart 6) are efficient catalysts for the homo- and copolymerization of butyl acrylate

Table 12. Nonaqueous Ethylene/1-Butene Copolymerization with Neutral Nickel Catalysts^a

complex	R ¹	R ²	R	yield (g)	activity ^b	incorp. (mol %)
8a	I	I	3,5-(CF ₃) ₂ C ₆ H ₃	4.3	1.1	4.2
8d	I	I	3,5-(CH ₃) ₂ C ₆ H ₃	10.0	2.5	4.1
9k	3,5-(CH ₃) ₂ C ₆ H ₃	3,5-(CH ₃) ₂ C ₆ H ₃	3,5-(CH ₃) ₂ C ₆ H ₃	2.7	0.7	4.3
5d	I	I	iPr	3.9	1.0	3.6

^aPolymerization conditions: toluene, 50 mL; complex, 40 μmol; ethylene, 2.0 MPa; $x_{\text{butene}} = 0.76$; 50 °C; 60 min. ^bIn the unit of 10⁵ g/mol_{Ni}·h.

Chart 6. Nickel Catalysts Used in Copolymerizations via Dual Radical/Catalytic Mechanism



(BuA), methyl methacrylate (MMA), and styrene.¹⁰¹ Drastically increased catalytic activities for the (co)polymerization are observed when PPh_3 is added. The reactivity ratios of the comonomers calculated by the Kelen–Tüdös method (terminal model) are very close to that reported for free radical copolymerization ($r_{\text{BuA}} = 0.19$, $r_{\text{Sty}} = 0.86$).^{102,103} Rather than the conventional coordination–insertion mechanism using neutral nickel catalysts, a dual radical/catalytic process is tentatively put forward. The homolytic cleavage of the Ni(II)–C bond is supposed to generate the radical initiators, which appears to be accelerated by the addition of PPh_3 . These results remind us to do more careful and convincing examinations when considering the (co)polymerization mechanism of polar monomers.

3. KETONE–IMINE NICKEL COMPLEXES

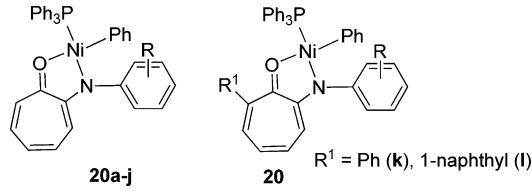
3.1. Ethylene Polymerization

3.1.1. Five-Membered-Ring Chelate Catalysts. While neutral nickel catalysts bearing six-membered chelate rings have been studied the most after the pioneering work of Grubbs et al., the development of catalysts with new chelate pattern is still

desirable, especially when six-membered chelate SHOP catalysts are found to be less active than five-membered ones.¹⁰⁴ Brookhart et al. reported catalysts **20a–l** (Table 13) bearing bulky 2-anilinotropones ligands that possess the virtues of both five- and six-membered chelate rings.

These complexes catalyze ethylene polymerization with high activities up to $10^7 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$.¹⁰⁵ The resultant PEs have an unprecedented range of branching numbers depending on ethylene pressure and reaction temperature (8–113 branches per 1000 carbons by use of complex **20b**). Introduction of either a phenyl or a naphthyl group into the 7-position of the 2-(2,6-diisopropylanilino)tropone ligand (**20k,l**) slightly increases the productivities and lifetimes at high temperature. Much longer half-life ($t_{1/2} > 1 \text{ h}$) and higher activities for the polymerization can be achieved at lower temperature (40 °C).¹⁰⁶ In 2003, Brookhart et al. reported five-membered-ring chelate neutral nickel catalysts **21a,b** (Table 14) based on bulky 2-anilinoperinaphthenones frameworks.¹⁰⁷ These catalysts display ethylene polymerization activities similar to those of the corresponding anilinotropone-based catalysts **20a–l**. Polymer branching can be controlled by variation of reaction temperature and ethylene pressure, and the chain transfer is supposed to be via a β -hydride elimination pathway by examining the correlation between ethylene pressure and polymer molecular weight. Under the reaction conditions employed, a decomposition of **21b** to free ligand is also observed, indicating that the catalysts are short-lived (half-life ca. 20–30 min, slightly longer than that of **20b**). Ethylene polymerizations with **20b** and **21b** are also run in the presence of PPh_3 to check their tolerance. Complex **20b** is not inhibited by adding 5 equiv of PPh_3 , and 50 equiv of PPh_3 can cause a 75% drop in catalytic activity. In contrast, a significant decrease in catalytic activity

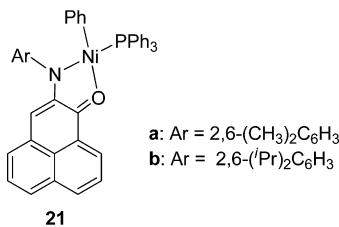
Table 13. Bulky 2-Anilinotropones Supported Nickel Catalysts for Ethylene Polymerization^a



complex	R	activity ($10^5 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$)	$M_n (\times 10^3)$	D_M	branches/1000C
20a	2,6-Me ₂	54.8	43	1.7	61
20a^b	2,6-Me ₂	24.1	— ^e	— ^e	— ^e
20b	2,6-iPr ₂	88.0	92	1.8	61
20b^b	2,6-iPr ₂	33.8	— ^e	— ^e	— ^e
20c	2-iBu	trace	18	2.1	72
20d	2-CH ₃ -6-iBu	10.1	115	2.0	73
20d^b	2-CH ₃ -6-iBu	3.4	— ^e	— ^e	— ^e
20e	2,6-Ph ₂	100.5	95	1.8	53
20f	2,6-Cl ₂	39.3	10	2.0	53
20f^b	2,6-Cl ₂	13.6	— ^e	— ^e	— ^e
20g	2,6-Br ₂	40.0	22	1.9	56
20g^b	2,6-Br ₂	14.8	— ^e	— ^e	— ^e
20h	F ₅	11.8	1.6 ^d	3.0	49
20i	2-Me	9.4	4.7 ^d	2.4	57
20j	2-Me-6-CF ₃	69.2	88	1.9	59
20j^b	2-Me-6-CF ₃	26.2	— ^e	— ^e	— ^e
20k^c	2,6-iPr ₂	108.0	— ^e	— ^e	76
20l^c	2,6-iPr ₂	87.2	56	2.2	70

^aPolymerization conditions: toluene, 200 mL; complex, ca. 5.2 μmol ; ethylene, 1.4 MPa; 80 °C; 10 min. ^b30 min. ^cComplex, 6.5 μmol . ^dDetermined by ¹H NMR. ^eNot reported.

Table 14. Anilinoperinaphthenone-Based Neutral Nickel(II) Catalyst for Ethylene Polymerization^a



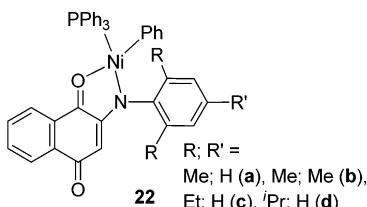
complex	TON ^f	M _w (×10 ³)	D _M	branches/1000 C
21a	8000	87.5	3.5	51
21b	47200	188.1	1.9	43
21b ^b	23700	167.4	2.7	46
21b ^c	62500	144.0	1.6	44
21b ^d	17900	144.0	1.8	36
21b ^e	3400	45.6	2.4	43

^aPolymerization conditions: toluene, 200 mL; catalysts, ca. 10 μmol; ethylene, 1.4 MPa; 80 °C; 30 min. ^b10 min. ^c60 min. ^d5 equiv of PPh₃ added. ^e50 equiv of PPh₃ added. ^fTON in the unit of mol ethylene/mol catalyst.

(ca. 65% reduction) for **21b** is observed with just 5 equiv of added PPh₃, while 50 equiv of PPh₃ leads to a ca. 93% reduction in catalytic activity.

Under atmospheric pressure of ethylene at 40 °C, anilinonaphthoquinone-based nickel complex **22** (Table 15)

Table 15. Five-Membered-Ring Chelate Anilinonaphthoquinone-Based Neutral Nickel Catalysts^a



complex	activity ^b	M _w (×10 ³)	D _M	branches/1000 C
22a	3.6	11.4	2.2	41
22b	4.2	14.4	2.4	32
22c	8.8	14.9	2.6	34
22d	13.2	71.1	4.0	21
22d ^c	9.6	933.1	2.9	7
22d ^d	2.5	4767.6	4.1	<1

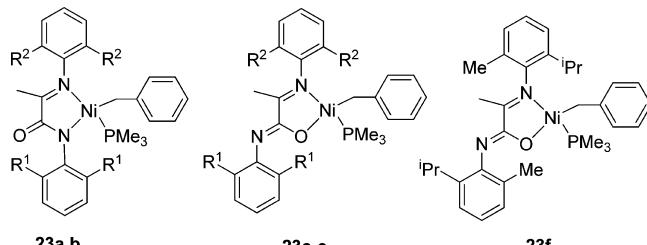
^aPolymerization conditions: toluene, 30 mL; catalysts, 5 μmol; 4 equiv of B(C₆F₅)₃; ethylene, 0.1 MPa; 40 °C. ^bIn the unit of 10⁵ g PE/mol_{Ni}·h. ^c20 °C. ^d0 °C.

activated with B(C₆F₅)₃ shows high activities for ethylene polymerization (up to 1.32×10^6 g PE/mol_{Ni}·h by use of **22d**). Branched or linear PEs are produced depending on the reaction temperature and bulkiness of the substituent.¹⁰⁸ It is also found that, for **22d**, PE with different branching structure can be obtained in the presence or absence of B(C₆F₅)₃.¹⁰⁹

α-Iminocarboxamide nickel complexes represent a family of five-membered chelate neutral nickel catalysts with unique copolymerization properties, which have recently been investigated using combinatorial chemistry approaches.¹¹⁰ In 2005, Bazan et al. first reported a group of neutral nickel catalysts **23a–f** containing α-iminocarboxamide ligands (Table 16).¹¹¹ Upon activation with Ni(COD)₂, these complexes have

been successfully employed in both ethylene polymerization and ethylene/functional monomer copolymerization.

Table 16. Nickel Complexes Containing α-Iminocarboxamide Ligands^a

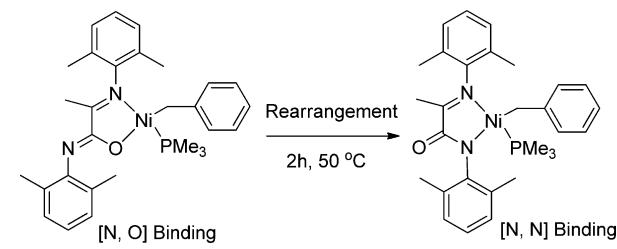


complex	R ¹	R ²	activity (10 ³ g/mol _{Ni} ·h)	M _n (×10 ³)	D _M
23a	H	iPr	77	oligomers	
23b	iPr	H	126	oligomers	
23c ^b	Me	Me	133	61	1.9
23d	Et	Et	784	7	5.0
23e	iPr	iPr	1302	7	6.1
23f ^b			210	76	1.7

^aPolymerization conditions: toluene, 30 mL; catalyst, 10 μmol; 2.5 equiv of Ni(COD)₂; ethylene, 0.7 MPa; 70 °C; 20 min. ^b20 °C.

It should be noted that both [N,O] and [N,N] coordination manners can be detected in the synthesis process. When the steric bulk is sufficiently large, as in **23d–f**, [N,O] binding is favored, while [N,N] products are generated in the case of smaller ligands (**23a** and **23b**). For **23c** with moderate steric effects, both [N,O] and [N,N] coordination modes are possible, and an irreversible rearrangement of [N,O] to [N,N] species occurs under 50 °C in 2 h (Scheme 4). The

Scheme 4. [N,O] and [N,N] Binding Modes for α-Iminocarboxamide Nickel Complex 23c

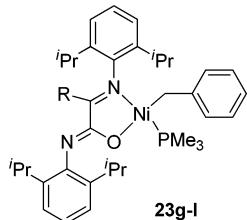


[N,N] structure is a thermodynamic product resulting from the electronic preference for nickel to bind to nitrogen over oxygen, while the [N,O] mode is kinetically preferred, probably due to the less bulky nature of oxygen moiety. Upon activation with 2.5 equiv of Ni(COD)₂, only the [N,O] complexes are effective for ethylene polymerization. Catalyst **23e** bearing the largest steric bulk around nickel produces PE with the narrowest molecular-weight dispersity ($D_M \approx 1.3$), and a linear dependence of the molecular weight versus time over a period of 30 min is observed.¹¹² This indicates the generation of long-lived active species during this process, in which several but not all of the characteristics of true living polymerization are satisfied.¹¹³ The relatively broad molecular-weight dispersity may result from entrapping of the catalysts by precipitated polymers or the slow initiation versus propagation, which would lead to the formation of a mixture of polymeric products to some extent.

This process is thus termed as a “quasi-living” polymerization.¹¹⁴

Bazan et al. also further synthesized a series of [N,O] neutral nickel complexes (**23g–l**) containing α -iminocarboxamide ligands to examine the effects of steric and electronic variations adjacent to the imine functionality (Table 17).¹¹⁵ Both the

Table 17. Influence of R Groups on Ethylene Polymerization Using Catalysts **23g–l^a**



complex	R	activity ^b	$M_n \times 10^3$	D_M
23e	Me	220	80	1.3
23g	Et	255	86	1.3
23h	CH ₂ CHMe ₂	420	121	1.4
23i	iPr	534	182	1.2
23j	Ph	259	102	1.2
23k	PhCF ₃ (p)	280	113	1.1
23l	PhOCH ₃ (p)	180	91	1.2

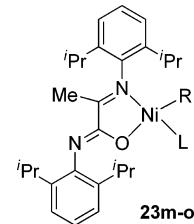
^aPolymerization conditions: toluene, 30 mL; catalyst, 10 μ mol; 2.5 equiv of Ni(COD)₂; ethylene, 0.7 MPa; 20 °C; 20 min. ^bIn the unit of 10^3 g PE/mol_{Ni}·h.

ethylene consumption rate and the molecular weight of the resulting PE increase with the bulk on the ligand framework, and the catalytic activity follows the order **23e** < **23g** < **23h** < **23i**. A greater than 2-fold increase in both catalytic activity and molecular weight of the polymer is observed using the isopropyl derivative **23i** (5.3×10^5 g PE/mol_{Ni}·h, $M_n = 1.8 \times 10^5$) as compared to the parent methyl species **23e** (2.2×10^5 g PE/mol_{Ni}·h, $M_n = 8.0 \times 10^4$). Moreover, lower electron density in the metal center results in higher ethylene polymerization activity (**23k** > **23j** > **23l**), but no discernible differences are observed in melting point (T_m) of the resultant polymers for all of these catalysts (ca. 127 °C). Significantly, similar to the aforementioned behavior for ethylene polymerization, nice performance (e.g., $D_M = 1.2\text{--}1.4$, linear dependence of time vs M_n) in ethylene/5-norbornene-2-yl acetate (NBA) copolymerization is also observed, which can be utilized to synthesize block copolymers (vide infra, section 3.3).⁴⁷

Complexes **23m–o** are readily obtained by the reaction of Ni(COD)₂, benzyl chloride, potassium salts of the ligands, and different additional stabilizing ligands.¹¹⁶ They are single-component catalysts for ethylene polymerization and the copolymerization of ethylene with functionalized norbornene monomers. As expected, complex **23n** is more readily initiated than the pyridine analogue **23m** due to the more labile nature of 2,6-lutidine (Table 18). Complex **23o** is sensitive to the functional groups in the monomers, and accordingly the polar norbornenes must be introduced after the initiation of ethylene in copolymerization.

On the basis of similar ligand structure, Bazan et al. designed novel binuclear nickel catalysts **24a** and **24b** (Chart 7) that have two nickel centers capable of initiating “quasi-living” polymerizations.¹¹⁷ Different from all of the other binuclear catalysts reported previously,⁴⁹ the two metal centers propagate

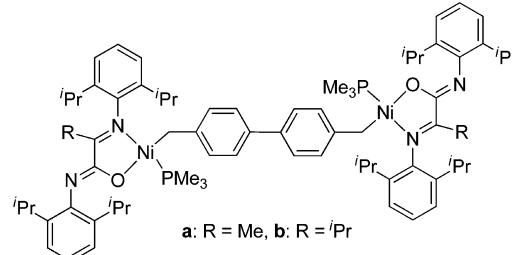
Table 18. Effects of Additional Stabilizing Ligand on Ethylene Polymerization^a



complex	R	L	activity ^c	$M_w \times 10^3$	D_M
23m	CH ₂ Ph	Py	60	63	1.8
23n	CH ₂ Ph	Lut	304	143	2.2
23o^b	(O=C)Ph	Py	270	145	1.7

^aPolymerization conditions: toluene, 30 mL; catalyst, 10 μ mol; 40 °C; 20 min; 0.7 MPa. ^b2.8 MPa. ^cIn the unit of 10^3 g PE/mol_{Ni}·h.

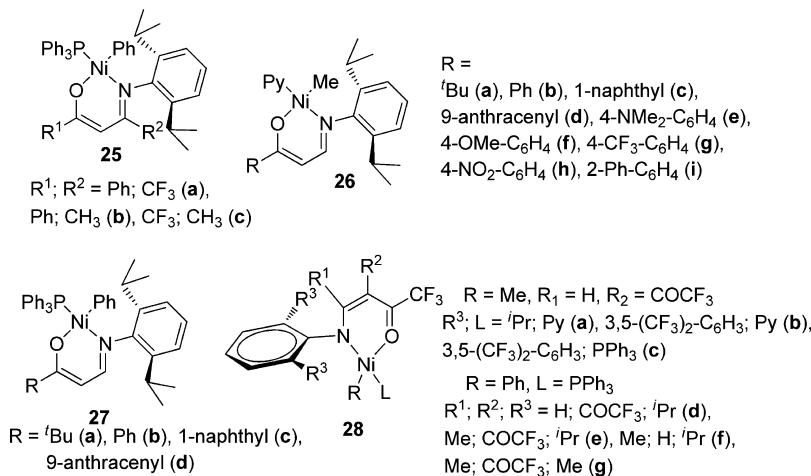
Chart 7. Binuclear Neutral Nickel Catalysts for the Production of Block Copolymers



away from each other as the telechelic copolymerization proceeds. The binuclear catalysts allow the synthesis of novel tri- and pentablock copolymer materials of ethylene and functionalized NBE, leading to improved mechanical properties over that produced by corresponding mononuclear analogues.¹¹⁷

3.1.2. Six-Membered-Ring Chelate Catalysts. In 2005, Li et al. reported catalysts **25a–c** (Chart 8) bearing β -ketiminato [N,O] ligands.¹¹⁸ They are active for ethylene polymerization at 60 °C in the presence of Ni(COD)₂. Introducing an electron-withdrawing group at the R¹ or R² position significantly increases the catalytic activity and the branch number of the resulting PE, and decreases the polymer molecular weight. For instance, complex **25a** with an electron-withdrawing $-CF_3$ group at R² position displays the highest activity of 8×10^4 g PE/mol_{Ni}·h and produces low M_w (3.4×10^3) PE with 125 branches per 1000 carbons. When the $-CF_3$ group at R² position is replaced by an electron-donating $-CH_3$ group, the activity lowers to 0.3×10^4 g PE/mol_{Ni}·h (**25b**), and the branch number also remarkably decreases (21 branches per 1000 carbon atoms), whereas the M_w of the resulting PE increases to 1.3×10^5 under similar conditions.¹¹⁸

Neutral nickel catalysts **26a–g** and **27a–d** (Chart 8) bearing β -ketiminato ligands were synthesized by Li et al. to systematically investigate ligand steric and electronic effects on the catalytic performance.¹¹⁹ The catalysts with bulky ligands are more active toward ethylene polymerization, producing PE with lower molecular weight and higher degree of branching. Catalyst **26g** with a strong electron-withdrawing group ($-CF_3$) shows an activity (1.9×10^6 g PE/mol_{Ni}·h) higher than that of the parent catalyst **26b** (8.7×10^5 g PE/mol_{Ni}·h·bar). In contrast, catalyst **26e** bearing a strong electron-

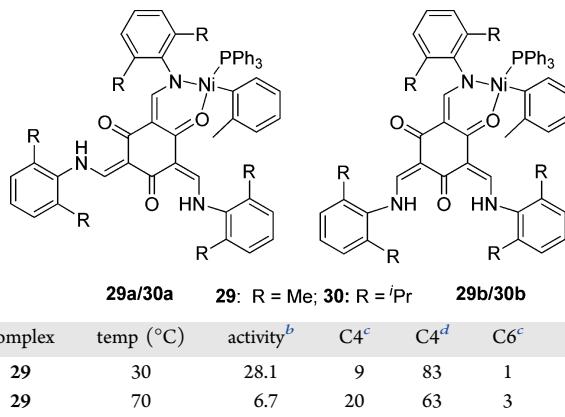
Chart 8. Six-Membered-Ring Chelate Neutral Nickel Catalysts Bearing β -Ketoiminato Ligands

donating $-\text{NMe}_2$ in the para position of the ligand is less active (1.6×10^5 g PE/mol_{Ni}·h). Additionally, the catalysts bearing electron-deficient ligands produce lower molecular weight polymer with enhanced degree of branching, due to the accelerated chain-walking reaction caused by the electronic perturbation of nickel(II) centers. A similar effect of the electron-withdrawing substituents has also been found for SHOP catalysts.^{120,121} Phosphine Ni(II)-Ph complexes **27a-d** show higher catalytic activities for ethylene polymerization than Ni(II)-Me complexes **26a-d**, which may originate from the different pendant ligands (PPh₃ vs Py) on the nickel centers.¹¹⁹

Neutral nickel catalysts **28a-c** (Chart 8) bearing electron-withdrawing trifluoromethyl (-CF₃) and trifluoroacetyl (-COCF₃) groups have been introduced by Mecking et al.¹²² Activated by either Ni(COD)₂ or B(C₆F₅)₃, these complexes polymerize ethylene to moderately branched PEs (generally in the range of 35–55 branches per 1000 carbons). Brookhart et al. reported phenyl nickel catalysts **28d-g** bearing PPh₃ ligand.¹²³ Among these complexes, **28d** is the most active and long-lived. A half-life over 15 h at 35 °C and an activity exceeding 10^7 g PE/mol_{Ni}·h are also observed. Productivity under standard conditions (200 psig, 60 °C, activated by Ni(COD)₂) follows the order **28d** > **28e** > **28f** ≈ **28g**. However, the rationale for the productivity differences is not clear.

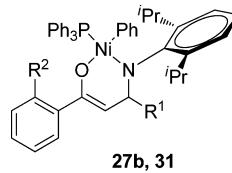
In 2009, single-component neutral nickel catalysts **29** and **30** (Table 19) derived from bulky salicylideneaniline ligands were developed by Kim's group.¹²⁴ The ligands retain the keto-enamine structure in complex state, and the metal centers exhibit a square planar structure based on the single-crystal XRD measurement. At 30 °C, they are highly active and selective for ethylene oligomerization, giving product with high butene content (beyond 90%). The highest record (96% of butene) under similar reaction conditions is achieved by catalyst **30**. The oligomerization selectivity markedly decreases at higher reaction temperature, indicative of their thermal instability. Less crowded complex **29** shows slightly higher activity (28.1×10^5 g oligomer/mol_{Ni}·h) than **30** (23.8×10^5 g oligomer/mol_{Ni}·h). Although it was not discussed by the authors, the high percentage (>80%) of 2-butene (internal olefin) in the dimerization product could be ascribed to the fast chain walking reactions.

Li et al. have devoted tremendous efforts to the exploration of the structure-activity relationship of neutral nickel

Table 19. Ethylene Oligomerization by Salicylideneaniline Nickel Complexes^a

^aOligomerization conditions: toluene, 40 mL; catalyst, 2.5 μmol; 30 min; 0.55 MPa; [MAO]/[Ni] = 200. ^bIn the unit of 10^5 g/mol_{Ni}·h. ^c α -Olefin. ^dInternal olefins.

catalysts.¹²⁵⁻¹²⁷ Complexes **27b** and **31a-d** (Table 20) bearing modified β -ketoiminato ligands are used to inspect the effects of R¹ and R² substituents on the catalytic behaviors toward ethylene polymerization.¹²⁵ With B(C₆F₅)₃ as an activator, all of these complexes display high activities. The electronic effects and steric hindrance of R¹ and R² greatly affect both molecular weight and branch content of the resulting PEs. As compared to the unsubstituted **27b** (R¹ = R² = H), complex **31a** (R¹ = H, R² = Ph) shows much higher activity up to 3.6×10^6 g PE/mol_{Ni}·h. Replacing the phenyl group at the R² position by a 1-naphthyl group (**31b**) does not improve catalytic activity. These results indicate that the aryl group at the R² position plays a leading role in protecting the active nickel species from the formation of the bis-ligated complexes, which are inactive toward ethylene polymerization.³³ Moreover, variation of R¹ group also results in a notable influence on catalytic activity. Similar to Brookhart's previous report,¹²³ introducing a substituent to the R¹ position leads to a negative effect on catalytic activity. For instance, surprisingly low activities of 1.4×10^5 g PE/mol_{Ni}·h for **31c** (R¹ = CH₃, R² = Ph) and 5.4×10^5 g PE/mol_{Ni}·h for **31d** (R¹ = CF₃, R² = Ph) are observed. Variations of R¹ and R² group also have remarkable influences

Table 20. Highly Active Nickel Catalysts Bearing Modified β -Ketoiminato Ligands^a

complex	R ¹	R ²	activity (10^5 g PE/mol _{Ni} ·h)	M_w ($\times 10^3$)	D_M	branches/1000C
27b	H	H	0.5	32.6	2.2	— ^c
31a ^b	H	Ph	36.3	26.5	1.9	20
31b	H	1-naphthyl	12.5	14.2	2.0	— ^c
31c	CH ₃	Ph	1.4	9.50	2.0	44
31d ^b	CF ₃	Ph	5.4	2.54	1.9	103

^aPolymerization conditions: toluene, 100 mL; complex, 20 μ mol; 1 equiv of B(C₆F₅)₃; ethylene, 2.5 MPa; 50 °C; 20 min. ^bComplex, 10 μ mol. ^cNot determined.

on molecular weight, branch content, and branch length of the produced PE. The molecular weight of the polymers decreases when substituent R² changes from hydrogen (27b) to phenyl (31a) to 1-naphthyl group (31b), while the branch degree concurrently increases. The R¹ group has a more significant influence on the branch structure of the produced polymers, allowing access to PEs varying from a relatively linear structure by 31a to a highly branched structure (ceraceous at ambient temperature) by 31d.

In 2010, another family of neutral nickel catalysts 32–34 (Table 21) based on cyclic β -ketiminato ligands was also

conjugated 33b,c and 34b,c produce PEs with much higher M_w ((2.9–5.7) $\times 10^4$) and lower branch contents versus the rigid, highly conjugated 33a and 34a (M_w = (7.5–9.8) $\times 10^3$). In addition, the pyridine stabilized catalysts 34a–c are less active than PPh₃ stabilized 33a–c due to the greater difficulties in catalyst activation, which is different from previous results.^{61,96}

Like for salicylaldimine systems, introducing a bulky substituent R¹ to the proximity of the phenoxy moiety is beneficial for the stability of the catalysts. Complexes 35, 36, and 26I thus designed show good activities for ethylene polymerization (Table 22),¹²⁷ and the formation of bis-ligated

Table 21. Highly Active Nickel Catalysts Bearing Modified β -Ketoiminato Ligands^a

			Ar = 2, 6-iPr ₂ C ₆ H ₃
32	33	34	a: n = 0 b: n = 1 c: n = 2
5.1	17.6	18.8	35.7
33.7	9.8	46.8	46.5
2.1	1.9	2.0	2.1
37	54	26	27
32	33a	33b	33c ^b
34a ^c	34b	34c ^c	

^aPolymerization conditions: toluene, 100 mL; catalyst, 20 μ mol; 20 min; ethylene, 5.0 MPa; 63 °C. ^bToluene, 70 mL; catalyst, 10 μ mol. ^cEthylene, 2.5 MPa. ^dIn the unit of 10^5 g/mol_{Ni}·h. ^eCalculated from ¹H NMR.

reported.¹²⁶ These conveniently accessible complexes are highly active toward ethylene polymerization without any activator. Under the optimized reaction condition, an activity of 3.6×10^6 g PE/mol_{Ni}·h is observed by use of 33c. In particular, the catalysts without bulky substituent still show high catalytic efficiency, which is quite different from the case for salicylaldimine systems. This has been explained by the low activation energies of 32 and 33a–c versus that of the typical salicylaldimine complex 4e according to DFT calculation results.¹²⁶ The ligand structure is also controlled to modulate the conjugation degree between the phenylene group and corresponding nickel chelate of 33a–c and 34a–c. The less

Table 22. Effects of R¹ Group in Neutral Nickel Catalysts on Ethylene Polymerization^a

			Ar = 2, 6-iPr ₂ C ₆ H ₃ Nor =
35a-b	36a-b	26b, 26I	
23.0	17.5	7.8	9.5
21.9	1.6	23.9	19.0
2.2	1.6	2.1	1.9
39	44	71	41
35b ^b	36b	26b ^c	26I ^c

^aPolymerization conditions: toluene, 100 mL; catalyst, 10 μ mol; 2 equiv of B(C₆F₅)₃; 20 min; ethylene, 5.0 MPa; 63 °C. ^bCatalyst, 20 μ mol. ^cCatalyst, 20 μ mol; ethylene, 2.5 MPa. ^dIn the unit of 10^5 g PE/mol_{Ni}·h. ^eCalculated from ¹H NMR.

complexes can be completely avoided. Furthermore, the tolerance of these sterically crowded catalysts toward additional pyridine is markedly improved (35a vs 34b, in Table 23).

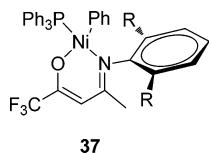
3.2. Norbornene Polymerization

Complexes 37a,b (Table 24) bearing β -enaminoketonato chelate ligands were reported by Jin et al. for the addition polymerization of NBE.¹²⁸ High catalytic activity up to 52.2×10^6 g PNB/mol_{Ni}·h (MAO/Ni = 5000) is observed when activated by MAO. Amorphous PNB with high M_w up to 4.8×10^6 is obtained by 37a (MAO/Ni = 3000) at 30 °C. Moreover, the Al/Ni ratio considerably affects not only the catalytic activity and polymer molecular weight, but also molecular-weight dispersity. In a range of Al/Ni = 2500–10 000, D_M

Table 23. Ethylene Polymerization in the Presence of Pyridine^a

complex	yield	activity ^c	$M_w \times 10^3$	D_M
34b	3.5	5.3	38.6	2.0
34b ^b	trace	— ^d	— ^d	— ^d
35a	10.2	15.3	15.3	1.9
35a ^b	3.0	4.5	13.3	1.9

^aPolymerization conditions: toluene, 100 mL; catalyst, 20 μmol ; 20 min; ethylene, 2.5 MPa; 63 °C. ^b5.0 equiv of pyridine was added. ^cIn the unit of 10⁵ g PE/mol_{Ni}·h. ^dNot determined.

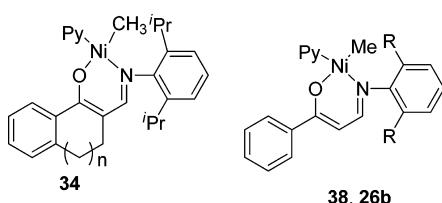
Table 24. Ketone–Imine Nickel Complexes/MAO for NBE Polymerization^a

complex	R	yield (%)	activity (10^6 g PNB/mol _{Ni} ·h)	$M_w \times 10^3$	D_M
37a	Me	92.2	52.2	2820	2.4
37a ^b	Me	14.6	8.2	2690	10.0
37a ^c	Me	87.2	49.2	1050	5.1
37a ^d	Me	71.6	40.4	2690	1.8
37b	iPr	83.0	46.8	2730	2.6

^aPolymerization conditions: chlorobenzene, 10 mL; catalyst, 0.2 μmol ; 5000 equiv of MAO; 100 000 equiv of norbornene; 30 °C; 10 min. ^b2500 equiv of MAO. ^c10 000 equiv of MAO. ^d60 °C.

values of the corresponding PNBS range from 5.1 to 10.0, except when Al/Ni = 5000 (D_M = 2.4).

Ni–Me pyridine catalysts 26b, 34a–c, 38, and a bis-ligated complex have been applied in NBE polymerization with $B(C_6F_5)_3$ as the sole cocatalyst (without the activation of organoaluminum compounds) (Table 25).¹²⁹ The ligand bend

Table 25. NBE Polymerization by Ketone–Imine Nickel Catalysts Activated by $B(C_6F_5)_3$ ^a

complex	n	R	yield (%)	$M_w \times 10^3$	D_M
34a	0		66	654	2.0
34b	1		69	458	2.1
34c	2		63	279	2.1
38		H	90	460	2.3
26b		iPr	81	532	1.9

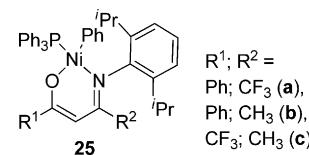
^aPolymerization conditions: toluene, 20 mL; catalyst, 3 μmol ; 6 equiv of $B(C_6F_5)_3$; ca. 5000 equiv of norbornene; 50 °C; 5 min.

angle displays great influence on polymer molecular weights, which decrease from 654×10^3 to 279×10^3 with the variation of catalyst structure from 34a to 34c. In addition, 26b and 38 are more active than 34a–c, and higher NBE conversion (90% and 81%, respectively) is observed under the same reaction conditions in 5 min. Molecular weight of the PNB produced by

38 is higher than that by 26b due to the decreased steric effect at the imine moiety. As expected, the bis-ligated complex exhibits a much lower catalytic efficiency, with a conversion rate as low as 31% even in the presence of a large amount of $B(C_6F_5)_3$.¹²⁹

3.3. Polar Monomer (Co)polymerization

Polar monomer MMA can be polymerized by complexes 25a–c (vide supra, Chart 8, Table 26). Syndiotactic-rich PMMAs (rr

Table 26. MMA Polymerization Catalyzed by Ketone–Imine Complexes 25a–c/MMAO System^a

complex	yield (%)	$M_v \times 10^3$	T_g^b (°C)	tacticity ^c		
				mm	mr	rr
25a	84.5	410	121.0	7.0	21.8	71.2
25b	98.7	470	121.8	7.9	26.9	65.2
25c	77.3	390	116.6	7.4	22.6	70.0

^aPolymerization conditions: toluene, 1.5 mL; complex, 5 μmol ; 150 equiv of MMAO; 750 equiv of MMA; 30 °C; 12 h. ^bDetermined by DSC. ^cCalculated from ¹H NMR.

around 70%) are obtained in excellent yields (>98%) upon the activation of MMAO.¹¹⁸ Among these complexes, 25b gives the highest monomer conversion (98.7%), followed by 25a (84.5%) and 25c (77.3%) under the same reaction conditions, implying a nonnegligible influence of electronic effects on the polymerization. The strong electron-withdrawing $-CF_3$ group, in either the R¹ or the R² position, considerably decreases the catalytic activity. The resultant PMMAs possess high molecular weights (M_v around 4×10^5) and high T_g around 118 °C.^{121,130,131} Note that highly efficient ethylene/MMA copolymerization promoted by neutral nickel catalysts can be achieved using 25a–c/MMAO (Table 27). Microstructure

Table 27. Ethylene/MMA Copolymerization by the 25a–c/MMAO System^a

complex	activity (10^3 g/mol _{Ni} ·h)	$M_w \times 10^3$	D_M	incorporation ^b (%)
25a	7.2	39.7	6.5	6.7
25b	17.7	99.0	4.1	0.8
25c	2.8	155	21.7	16.7

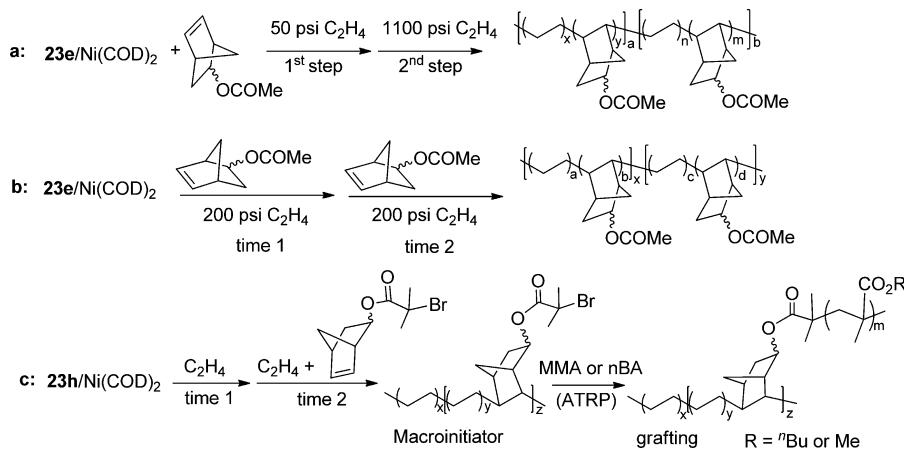
^aPolymerization conditions: toluene, 40 mL; catalyst, 50 μmol ; 150 equiv of MMAO; 750 equiv of MMA; ethylene, 2.0 MPa; 25 °C; 2 h.

^bDetermined by high-temperature ¹H NMR at 120 °C.

analysis reveals long ethylene sequences with isolated MMA units in the backbone, and the MMA incorporation in the copolymer ranges from 1 to 17 mol %. A predominant ethylene-initiated/ethylene-terminated polymer structure is confirmed by NMR data. The mechanism studies of the ethylene/MMA copolymerization catalyzed by 25a–c/MMAO support a coordination–insertion mechanism.

Catalytic system 23e/Ni(COD)₂ (Table 16) developed by Bazan's group exhibits unique features for both ethylene polymerization and the copolymerization of ethylene with 5-norbornene-2-yl acetate (NBA) (vide supra).^{111,112,115} During

Scheme 5. Syntheses of Block Copolymers Using Bazan's Catalysts

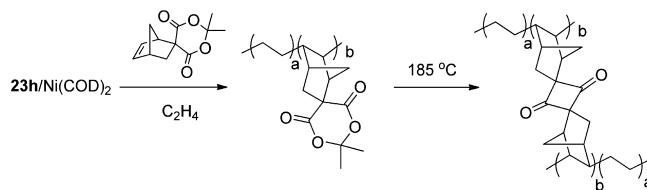


the (co)polymerizations, narrow molecular-weight dispersity and an increase of M_n with time are observed.¹¹² This indicates a tendency of living polymerization, although it does not meet all of the conditions of truly living polymerization.¹¹³ The catalyst system is also effective for ethylene/5-norbornene-2-ol (NBO) copolymerization but not via a living manner, producing copolymers with the hydroxyl functionalities homogeneously distributed throughout the copolymer main chain.⁶³

Taking advantage of the unique property of this system, different types of block copolymers have been prepared.^{132–135} Block copolymers containing segments of ethylene and NBA with different molar compositions have been synthesized by a simple procedure that involves an ethylene pressure jump (Scheme 5a).¹³² All of the products have D_M values between 1.3 and 1.6. Microphase separation of the two blocks with different molecular composition is clearly observed by TEM examination. In a one-pot semibatch copolymerization of ethylene with NBA, ethylene is added continuously, while NBA comonomer is consumed as the copolymerization proceeds. As a result, a tapered copolymer is formed in which the ethylene/NBA ratio acts as a function of chain length.¹³³ A polymer chain resembling tetrablock copolymer can be obtained by injecting additional NBA comonomer after time 1 (Scheme 5b).¹³⁴ Molecular weight, block length, and thermal properties of the copolymer can be easily adjusted by changing the reaction time (time 1, time 2) and comonomer concentration in feed. These amorphous and semicrystalline alternating block copolymers, especially those without microphase separate, have much better elastomeric properties at 65 °C than at 20 °C. By sequential addition of the monomers, a PE macroinitiator can be prepared using $23h/\text{Ni}(\text{COD})_2$ (Scheme 5c) with excellent control over the copolymer architecture.¹³⁵ Copolymerization of ethylene with monomer 5-norbornen-2-yl-2'-bromo-2'-methyl affords a macroinitiator that further initiates the following ATRP reactions of MMA. Semicrystalline graft copolymers PE-graft-PMMAAs with well-defined microstructures (PMMA content = 2–60 mol %) are easily obtained and are expected to be further utilized as a blend compatibilizer for linear PE with other polar polymers.¹³⁵ Grafting *n*-butyl acrylate (*n*BA) to the aforementioned macroinitiator leads to a much softer acrylate-containing polyolefin elastomer (Scheme 5c). An elongation at break of 780% and a recovery of 83% at 400% strain are achieved.¹³⁶

Bazan and Hawker et al. designed a polar norbornene monomer bearing Meldrum's acid functionality. Effective copolymerization of this monomer with ethylene by $23h/\text{Ni}(\text{COD})_2$ affords semicrystalline copolymers with controllable comonomer incorporation (Scheme 6).¹³⁷ The Meldrum's acid

Scheme 6. Ketene Functionalized PE Production and Its Cross-linking



moieties in the polymer material are readily converted to ketene groups by heating. The dimerization of the ketene groups under these conditions results in cross-linking of the functionalized PE. This method allows control over the cross-linking density and thus the property of the resultant polymeric material by manipulation of polar NBE incorporation.

As demonstrated previously,^{85,86} vinyl-type PNB is one kind of promising polymeric material. However, high melting points and poor solubility of pure PNB in common organic solvent make it difficult to process. To improve the physical performance, functional groups have been effectively introduced to the polymer chains by the direct copolymerization approach.¹²⁹ With low dosage $\text{B}(\text{C}_6\text{F}_5)_3$ as activator, **26b**, **34a–c** are able to copolymerize NBE with NBA or 5-norbornene-2-yl-methanol (NBM). Monomer conversion as high as 96% is achieved in 10 min using **34b** for NBE/NBA copolymerization, while 81% conversion is observed by **34a** in the NBE/NBM copolymerization. This facile copolymerization process efficiently yields functional copolymers with different molecular weight ($M_n = (4.2–14.4) \times 10^4$ for NBE/NBA copolymers and $(1.6–9.3) \times 10^4$ for NBE/NBM copolymers) and comonomer incorporation (6.3 mol % of NBA and 11.2–21.8 mol % of NBM, respectively).

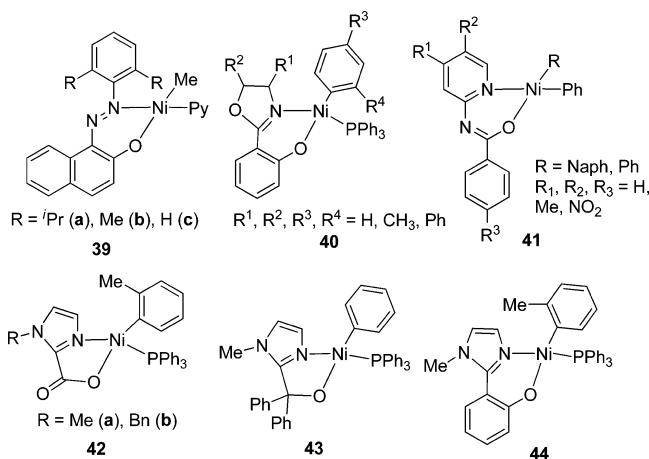
4. OTHER BIDENTATE NEUTRAL NICKEL CATALYSTS

4.1. Other κ^2 -[N,O]Ni Catalysts

[N,O] chelate ligands other than phenoxy-imine and ketone-imine frameworks have also been used to synthesize neutral

nickel catalysts.^{138–143} Complexes **39a–c** (Chart 9) with chelating diazene ligands are activator-free catalysts for ethylene

Chart 9. Previously Reported $\kappa^2\text{[N,O]} \text{Ni}$ Catalysts

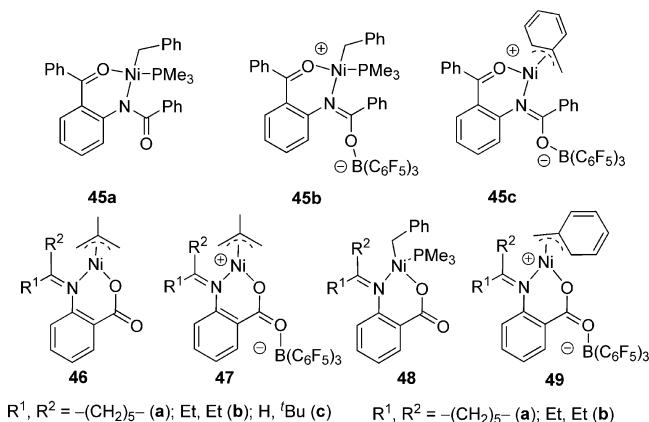


polymerization. **39a** bearing bulky substituted ligand provides high molecular weight, moderately branched PE at reasonable rates, whereas **39b,c** oligomerize ethylene under similar reaction conditions.¹³⁸

Complexes **40** (Chart 9) bearing 2-oxazolinylphenolato ligands oligomerize ethylene and propylene in the presence of organoaluminum cocatalysts (MAO, AlEt₃, iBu₂AlH) or phosphine scavenger Ni(COD)₂.^{139,140} The oligomers obtained by these complexes mainly consist of low carbon olefins (C₄–C₈). The highest activity of 5.5×10^5 g oligomer/mol_{Ni}·h and 83% selectivity of C₆ internal olefins are achieved by **40a** (R¹–R⁴ = H)/MAO. For propylene oligomerization, complex **40a** exhibits the highest activity when combined with MAO (1.3×10^5 g oligomer/mol_{Ni}·h). As single-component catalysts, **42–44** (Chart 9) containing [N,O] bidentate ligands convert ethylene to either oligomer (by **42a,b** and **43**) or polymer (by **44**) as the main product under moderate pressures.¹⁴¹ N-(2-Pyridyl)benzamide nickel complexes **41**/MAO oligomerize ethylene to high content of C₄ and C₆ oligomer products with activities up to 4.94×10^5 g/mol_{Ni}·h.¹⁴⁴

Lee et al. reported a series of N-(2-benzoylphenyl)-benzamido nickel catalysts **45a–c** (Chart 10).¹⁴⁵ The reaction of B(C₆F₅)₃ with complex **45a** affords **45b** or **45c** depending on

Chart 10. $\kappa^2\text{[N,O]} \text{Ni}$ Complexes Coordinated with Different Ligands



R¹, R² = -(CH₂)₅– (a); Et, Et (b); H, iBu (c)

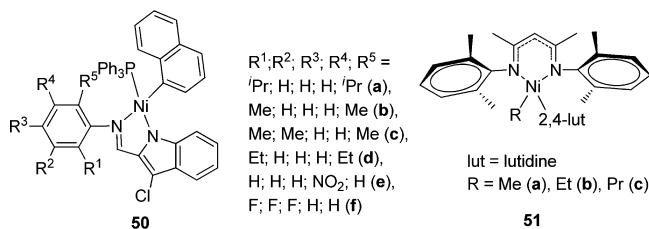
R¹, R² = -(CH₂)₅– (a); Et, Et (b)

how many equivalents of the borane is added. Neither **45a** nor **45b** bearing trimethylphosphine ligand is effective toward ethylene polymerization, whereas the base-free **45c** is moderately active to yield low molecular weight branched PE. The reaction of **46a–c** with 1 equiv of B(C₆F₅)₃ gives zwitterionic complexes **47a–c** that are active for ethylene polymerization. This is an interesting result considering that the corresponding complexes bearing 2-(diphenylphosphino)-benzoato and 2-(diphenylamino)benzoato ligands only dimerize ethylene. As expected, the η^3 -benzyl complexes **49a** and **49b** (prepared from the reaction of **48a** and **48b** with B(C₆F₅)₃) are highly active for ethylene polymerization to give low M_w (ca. 10⁴) highly branched PE.¹⁴⁶

4.2. $\kappa^2\text{[N,N]} \text{Ni}$ Catalysts

Some nickel complexes containing [N,N] chelate ligands are useful in ethylene oligomerization. Without activators, the imino-indole complexes **50a–f** (Chart 11) are effective

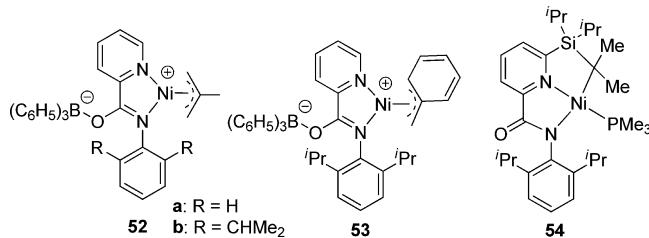
Chart 11. $\kappa^2\text{[N,N]} \text{Ni}$ Catalysts for Ethylene Oligomerization



ethylene oligomerization catalysts (2.1×10^4 g oligomer/mol_{Ni}·h by use of **50e**).¹⁴⁷ The nature of the ligands has a major influence on the catalytic activity (**50e** > **50c** > **50b** > **50d** > **50f** > **50a**). The activity of **50b** at 80 °C is almost doubled as compared to that at 15 °C, and the content of C₄ product in the resulting oligomer is also increased at higher temperature. Ethylene is found to slowly insert into the monoalkyl complexes **51a–c**, giving highly branched short-chain ethylene oligomers.¹⁴⁸ Warren and Strassner et al. successfully isolated and characterized the lutidine-free, neutral β-agostic species by single-crystal X-ray and computational studies.¹⁴⁹

Bazan et al. synthesized [N,N] coordinated pyridinecarboxamido nickel catalysts **52–54** (Chart 12), which are

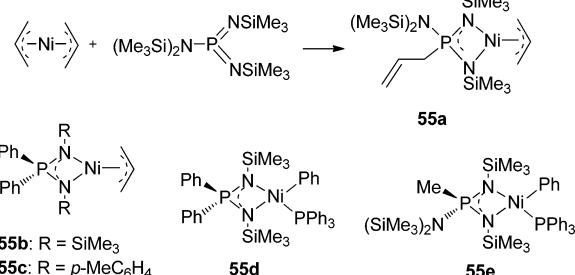
Chart 12. $\kappa^2\text{[N,N]} \text{Ni}$ Complexes Reported by Bazan et al.



isoelectronic to α -iminocarboxamide complexes.¹⁵⁰ Catalyst **53** is far more active than **52a,b**, probably as a result of faster initiation of η^3 -benzyl nickel complexes. This is consistent with that found by Johnson et al. in their early work.³⁴ An attempt to introduce more steric bulk, however, leads to the formation of deactivation product **54** by C–H activation of one isopropyl group.

Back in the 1980s, Keim et al. reported the synthesis of catalyst **55a** by the *in situ* reaction of $\text{Ni}(\text{COD})_2$ or $(\eta^3\text{-allyl})_2\text{Ni}$ with aminobis(imino)phosphorane ligand (**Scheme 7**). This catalyst polymerizes ethylene to branched PE with

Scheme 7. In Situ Generated and Well-Defined Iminophosphonamide Nickel Catalysts



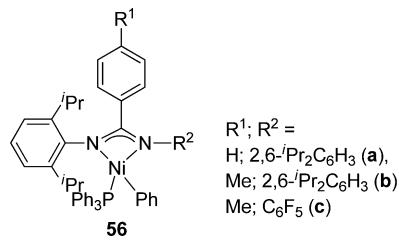
physical properties resembling that of high-pressure PE, which is of commercial interest.^{151,152} According to Fink et al., the same system is also active for α -olefin polymerization. Branched polymer with the monomers enchain in 2, ω -coupling pattern is obtained, which is explained by a so-called “migration mechanism”.^{153,154}

The pure discrete $(\eta^3\text{-allyl})\text{Ni}$ iminophosphoamide (PN_2) complexes **55a–d** (**Scheme 7**) are not effective for ethylene oligomerization or polymerization, while **55a** generated *in situ* in the presence of 450 psig of ethylene produces high molecular weight branched PE (ca. 30–40 branches per 1000 carbon atoms). This suggests that the active species is $\text{Ni}(0)$ –alkene complex performed or generated *in situ* by the decomposition of $(\eta^3\text{-allyl})_2\text{Ni}$.^{155,156} In the presence of excess MAO, complexes **55a–d** are extremely active for ethylene dimerization (10^6 – 10^7 g dimmer/mol_{Ni}·h), whereas **55d** produces branched oligomers ($M_n = 530$, about 80 methyl branches per 1000 carbon atoms) with low catalytic activity (100–1000 g oligomer/mol_{Ni}·h) with the help of stoichiometric Rh(acac) $-(\text{C}_2\text{H}_4)_2$.¹⁵⁵ In addition, **55d** is active for 1-hexene isomerization without any activator, affording 2- and 3-hexene. Note that the hard Lewis base PN_2 ligands with low steric hindrance are also susceptible to abstraction by hard Lewis acidic organoaluminum activators or $\text{B}(\text{C}_6\text{F}_5)_3$. Complex **55e** oligomerizes ethylene to branched polymer at a very low activity (2 g oligomer/mol_{Ni}·h) in the absence of any phosphine scavenger. The activity can be improved by adding 10 equiv of $\text{Ni}(\text{COD})_2$ (42.5 g oligomer/mol_{Ni}·h). NMR data reveal an oligomer microstructure similar to that provided by the mixture of $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)_2$ and $\text{Ni}(\text{COD})_2$ or $(\eta^3\text{-allyl})_2\text{Ni}$.¹⁵⁶

Catalysts **56a–c**/MAO promote ethylene oligomerization to give mainly dimers (ca. 65%) and trimers (ca. 35%) (**Table 28**).¹⁵⁷ The structure of nickel complexes only slightly affects the catalytic activity. As for NBE polymerization, bulky catalysts **56a** produce polymers with the highest molecular weight, whereas **56c** with an electron-withdrawing pentafluorophenyl group shows the highest catalytic activity.

When activated by MMAO, nickel complexes **57a–d** (**Table 29**) bearing nonsymmetric bidentate pyrrole-imine chelate ligands display very high activities toward vinyllic polymerization of NBE.¹⁵⁸ **57c–d** bearing less bulky ligands exhibit catalytic activities greater than 4.3×10^7 g PNB/mol_{Ni}·h, while **57a** containing two bulky substituents is the least active. This

Table 28. $\kappa^2\text{-[N,N]Ni}$ Complexes Coordinated with Monoamidinate Ligands

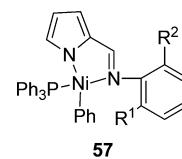


complex	monomer	activity (10^4 g/mol _{Ni} ·h)	distribution of oligomers		
			C ₄	C ₆	C ₈ –C ₁₂
56a^a	ethylene	12.9	63.4	36.0	0.6
56b^a	ethylene	12.0	68.5	31.5	
56c^a	ethylene	16.0	63.9	36.1	
complex	monomer	activity (10^4 g/mol _{Ni} ·h)	$M_w (\times 10^3)$	D_M	
56a^b	NBE	950	854.3	2.6	
56b^b	NBE	970	716.4	2.5	
56c^b	NBE	1550	520.9	2.7	

^aEthylene oligomerization conditions: toluene, 20 mL; catalyst, 15 μmol ; MAO/Ni = 600; ethylene, 0.05 MPa; 20 °C; 0.5 h.

^bNorbornene polymerization conditions: toluene, 25 mL; catalyst, 1 μmol ; MAO/Ni = 600; norbornene, 4 g; 40 °C; 10 min.

Table 29. $\kappa^2\text{-[N,N]Ni}$ Complexes for NBE Polymerization^a



complex	R ¹	R ²	yield (%)	activity (10^7 g PNB/mol _{Ni} ·h)	$M_v (\times 10^3)$
57a	ⁱ Pr	ⁱ Pr	67	3.9	650
57b	ⁱ Pr	Me	70	4.0	670
57c	Et	Et	74	4.3	690
57d	^t Bu	H	77	4.4	710

^aPolymerization conditions: toluene, 30 mL; catalyst, 0.5 μmol ; MMAO/Ni = 2000; norbornene, 2.4 g; 30 °C; 5 min.

indicates a possible blockage of NBE insertion by the large substituents ortho to the imine nitrogen.

N-Arylcyanoo- β -diketiminato methylly neutral nickel complexes **58a–61a** (**Chart 13**)¹⁵⁹ are found to be inactive toward ethylene polymerization, probably because of strong coordination of methylly group to nickel center. Coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ with the cyan groups in **58a–61a** leads to the formation of novel complexes **58b–61b**. Catalysts **58b** and **59b** are found to oligomerize ethylene, while **60b** and **61b** provide polymers, and additional $\text{B}(\text{C}_6\text{F}_5)_3$ is found to accelerate these reactions.¹⁶⁰ The resultant polymers possess moderate molecular weights with mainly isolated methyl branches.

4.3. $\kappa^2\text{-[P,N]Ni}$ Catalysts

To date, only limited research has dealt with neutral nickel catalysts bearing [P,N] chelating ligands.^{161–164} Sterically congested phosphino-sulfonamide nickel complexes **62a–h** (**Chart 14**) have been reported by Brookhart's group to be active in a variety of solvents, giving branched ethylene oligomers.¹⁶¹ The parent catalyst **62a** (R = Ph) displays activities around 10^5 g oligomer/mol_{Ni}·h, affording oligomers with 17–35 branches per 1000 carbon atoms. Complex **62b**

Chart 13. κ^2 -[N,N] Nickel Complexes with Cyan Groups and Their Activations by $B(C_6F_5)_3$

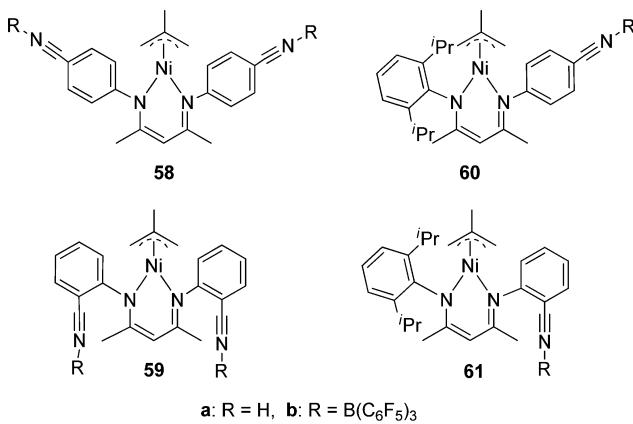
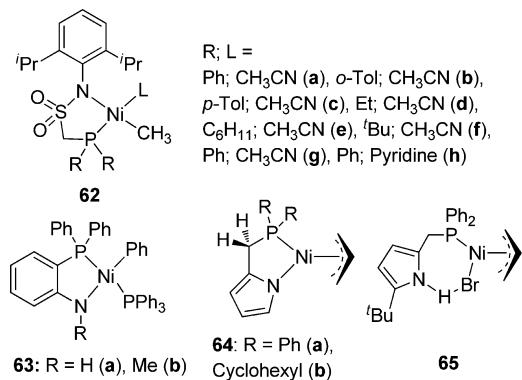


Chart 14. Neutral Nickel Catalysts Based on [P,N] Chelate Ligands



containing bulkier *o*-tolyl substituents shows slightly lower catalytic activities. **62e** bearing electron-rich cyclohexyl substituents is a longer-lived catalyst, affording products with a substantially higher degree of polymerization and branching degree. NMR experiments reveal that the branches originate from the isomerization of the nickel alkyl species during chain propagation rather than reincorporation of α -olefin products.

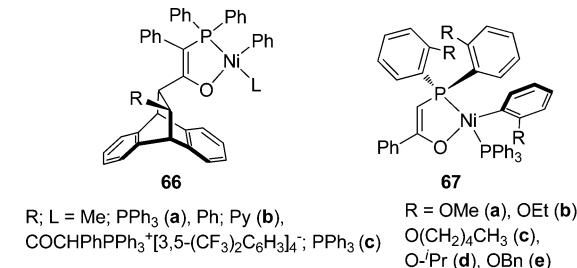
In the presence of MAO, nickel complexes **63a,b** polymerize NBE with high activity up to 4.4×10^7 g PNB/mol_{Ni}·h. The addition type PNB has high molecular weight ($M_w = 3.1 \times 10^7$ by **63a**) and moderate molecular-weight dispersity ($D_M = 2.3 - 3.9$).¹⁶³ Complexes **64** and **65** are synthesized by the reaction of potassium salts of 2-phosphinomethyl-1*H*-pyrroles, K-[R₂PCH₂C₄H₃N] (R = Ph, Cy), with (η^3 -allyl)nickel bromide.¹⁶⁴ Addition of $B(C_6F_5)_3$ to **64a** or **64b** causes an electrophilic attack in 5-position of the pyrrole ring to afford the zwitterions (η^3 -C₃H₅)Ni[NC₄H₃(2-CH₂PR₂)-5-B(C₆F₅)₃]. This catalyst promotes the isomerization of 1-hexene to predominant *E*-hex-2-ene at room temperature in high conversions (>90%).

4.4. κ^2 -[P,O]Ni Catalysts

Bulky substituents in α -diimine²⁰ and salicylaldimine³⁴ nickel catalysts strongly influence the polymerization characteristics, and the rationale is sometimes also applicable to [P,O] catalysts. In 2001, Gibson et al. reported the effect of bulky substituents on olefin polymerization behavior of [P,O] nickel catalysts.¹⁶⁵ A dramatic increase in the catalytic activity for ethylene polymerization is observed by incorporating bulky

substituents adjacent to the oxygen donor site of **66a–c** (Chart 15). Upon activation with Ni(COD)₂, the phosphonium-

Chart 15. Previously Reported Phosphino–Enolate Neutral Nickel Catalysts



containing complex **66c** achieves a catalytic activity of 3.5×10^7 g PE/mol_{Ni}·h. Moreover, these complexes are also able to oligomerize propylene and 1-hexene. Similar to **66c**, catalyst **66a** oligomerizes propylene at 4 bar, 70 °C, with an activity of 1.4×10^6 g/mol_{Ni}·h to give a Schultz–Flory distribution ($K = 0.64$) of C₆–C₄₈ olefins. Both complexes oligomerize 1-hexene to C₁₂–C₃₆ oligomers with relatively low activities. The authors ascribed the increase in catalytic activity to the presence of bulky anthracenyl-derived substituent next to the oxygen donor site, which can protect the electrophilic nickel center from binding potentially poisoning donor groups. The bulky substituent may also disfavor the coordination of the other nickel center to the oxygen site, which results in ligand migration and the formation of a catalytically inactive bis-ligated species. Notably, low molecular weight ($M_n = (2.6 - 3.8) \times 10^3$) functionalized PE with MMA end group is obtained by the copolymerization of ethylene with MMA.¹⁶⁶ Since then, neutral nickel catalysts based on phosphino–enolate ligands have rarely been reported for ethylene polymerization. Until recently, a family of nickel complexes **67a–e** (Chart 15) based on benzoylmethylenetri(2-alkoxylphenyl)phosphorane was found to be sufficiently robust catalysts for ethylene polymerization upon treatment with Ni(COD)₂. Highly linear low molecular weight ($M_v = 1100 - 5500$ g/mol) PE containing mainly terminal double bonds is obtained.¹⁶⁷ The existence of 2-alkoxyl-aryl substituents on the phosphorus atom is found to improve the catalytic activities. Catalyst **67d** achieves the highest catalytic activity of 2.1×10^6 g PE/mol_{Ni}·h, which is 1 order of magnitude higher than that of the corresponding SHOP catalyst.³⁰

Well-defined phosphino–phenolate neutral nickel catalysts **68a–f** were reported by Li et al. to be active for ethylene polymerization. These complexes (Table 30) produce low molecular weight linear PE as single-component catalysts.^{168,169} Complex **68a** with low steric bulk at the ortho position of the phenoxy moiety is less active for ethylene polymerization, which is reasonable for neutral nickel catalysts. While introducing *tert*-butyl (**68b**) or phenyl (**68c**) group can significantly improve ethylene polymerization activity, no obvious difference is observed by further increasing the steric hindrance (**68d**, 9-anthracyl), which is different from salicylaldimine systems. Although the electronic effect of the substituent R may influence catalytic activity (**68e**), the catalytic process is clearly more sensitive to the variation of phosphanyl moiety. For example, **68f** with a *tert*-butyl group at the phosphorus atom is more readily initiated than its diphenyl analogue.

Table 30. Well-Defined Phosphino–Phenolate Nickel Catalysts for Ethylene Polymerization^a

complex (μmol)	R	ethylene (MPa)	activity ($10^3 \text{ g PE/mol}_{\text{Ni}} \cdot \text{h}$)	$M_w (\times 10^3)$	D_M	68a–e	68f
						68a–e	68f
68a (24)	H	3.0	40	5.3	2.0		
68b (10)	^t Bu	1.0	9780	7.8	2.0		
68c (31) ^b	Ph	3.0	4460	7.9	2.3		
68d (23)	9-anthracyanyl	1.6	3450	6.8	2.7		
68e (10)	C ₆ F ₅	1.0	6540	5.9	2.1		
68f (10)		1.0	10860	3.7	2.2		

^aPolymerization conditions: toluene, 100 mL; 70 °C; 20 min. ^b80 °C.

Complexes **68b,e,f** are chosen to catalyze NBE polymerization in the presence of a low dosage of B(C₆F₅)₃ as the sole cocatalyst (Table 31).¹⁶⁹ High molecular weight (>10⁶ g PNB/mol_{Ni}·h).

Table 31. NBE Polymerization by Complex **68**/B(C₆F₅)₃ Systems^a

complex	conversion (%)	activity ^b	$M_w (\times 10^3)$	D_M
68b	98.6	4.59	1201	1.8
68e	90.5	4.24	1220	1.8
68f	87.3	4.09	1162	1.8

^aPolymerization conditions: toluene, 20 mL; catalyst, 2 μmol ; 3 equiv of B(C₆F₅)₃; C_(norbornene) = 0.416 mol/L; 60 °C; 5 min. ^bIn the unit of 10⁶ g PNB/mol_{Ni}·h.

polymers are obtained, and a monomer conversion as high as 98.6% in 5 min is observed by using **68b**, which is far more efficient than bis-ligated complexes and previously reported catalysts.^{129,170} NMR evidence indicate a possible transfer of C₆F₅ group from B(C₆F₅)₃ to nickel in the catalytic process.

In view of the unique feature of phosphine–sulfonate palladium catalysts, their nickel analogues have also been examined for ethylene polymerization. The first well-defined neutral nickel catalysts supported by phosphine–sulfonate ligands (**69a–c**) were synthesized and structurally characterized by Rieger et al.¹⁷¹ In the presence of phosphine scavengers, these catalysts produce PEs with 15–25 branches per 1000 carbon atoms. Similar results in terms of catalytic activity, molecular weight, and branch number of the resultant PEs are obtained by **69b** and **69c**, while the unsubstituted **69a** yields only a trace amount of polymer (Table 32). In the presence of MMA, **69b** gives polymer with slightly higher molecular weight but narrow molecular-weight dispersity ($D_M = 1.3$) in low activity. However, no data have been provided regarding the copolymer structure or MMA incorporation. Although the palladium analogues are efficient catalysts for the copolymerization of various polar comonomers with ethylene, phosphine–sulfonate nickel catalysts reported here are killed by methyl acrylate (MA).¹⁷¹

To facilitate mechanism investigation and avoid the use of phosphine scavengers that are prone to reacting with the ligands,^{150,172} Jordan et al. prepared base-free complexes **70b** and **70c**.¹⁷³ As compared to **70a** that stabilized by PPh₃ ligand, base-free **70b** produces higher molecular weight ($M_n = 1300$) PE containing 11 methyl branches per 1000 carbon atoms with much higher activities (Table 33). **70c** is less active than **70a**,

Table 32. First Well-Defined Phosphine–Sulfonate Neutral Nickel Catalysts^a

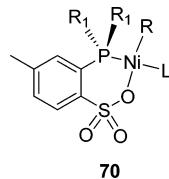
complex	R	time	activity ($10^3 \text{ g/mol}_{\text{Ni}} \cdot \text{h}$)	M_w	D_M
69a	Ph	60	trace	— ^d	— ^d
69b^b	2-OMeC ₆ H ₄	10	425	1200	1.3
69b^c	2-OMeC ₆ H ₄	60	100	2100	1.3
69c	2-MeC ₆ H ₄	20	790	950	2.0

^aPolymerization conditions: toluene, 50 mL; complex, 25 μmol ; 2 equiv of B(C₆F₅)₃; 2.0 MPa; at room temperature. ^bComplex, 50 μmol . ^c80 °C; 20 mL of MMA was added. ^dNot determined.

affording higher molecular weight ($M_n = 2100$) PE with fewer branches (1 methyl branch per 1000 carbon atoms) and higher fraction of terminal olefin units (91%).

Allylnickel complexes **71a,b** were reported by Nozaki et al. to be active for ethylene polymerization without any activator (Table 34), producing low molecular weight PEs with only methyl branches (8–13 methyl branches per 1000 carbon atoms).¹⁷⁴ Chen et al. found that **71a–c** are only slightly active for NBE polymerization, but a significant increase in activity can be achieved by the addition of 1 equiv of B(C₆F₅)₃.¹⁷⁵ Complexes **71a–d** are also active for the copolymerization of ethylene with NBE, which can not be accelerated by B(C₆F₅)₃. This is different from that observed in homopolymerization, implying a possible different polymerization mechanism of this catalytic system toward the two monomers in the presence of B(C₆F₅)₃.

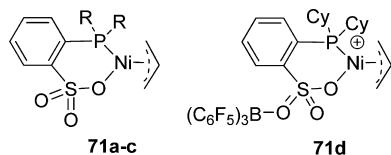
The first example of high molecular weight PE produced by phosphine–sulfonate neutral nickel catalyst was reported by Mecking et al.¹⁷⁶ Reaction medium is found to control the ethylene polymerization with highly active catalysts **72a–c** (Table 35), affording PEs from low M_n (<800) branched polymer (>15 branches per 1000 carbon atoms) to high M_n (>1.8 × 10⁵) linear product (<1 branches per 1000 carbon atoms). Scott et al. introduced a bulky Ar (2-(2',6'-(OCH₃)₂C₆H₃)C₆H₄) group into the ligand (Table 36, **73b,c**) to improve the molecular weight of the polymer using phosphine–sulfonate nickel catalysts.¹⁷⁷ With two Ar sub-

Table 33. Ethylene Polymerization by Base-Free Phosphine–Sulfonate Nickel Benzyl Complexes^a

complex	R ¹	R	L	activity (10^3 g PE/mol _{Ni} ·h)	M_n^b	Me ^c branches	ter/int ^d
70a	2-OMeC ₆ H ₄	Ph	PPh ₃	30	760	9	68/32
70b	2-OMeC ₆ H ₄	η^3 -benzyl		140	1300	11	35/65
70c	Cy	η^3 -benzyl		11	2100	1	91/9

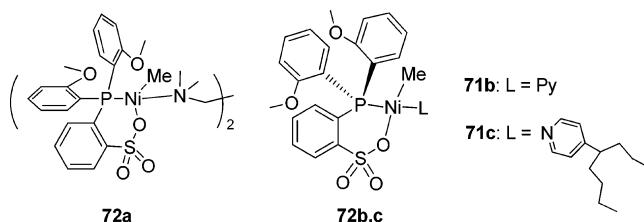
^aPolymerization conditions: toluene, 25 mL, CH₂Cl₂, 5 mL; complex, 20 μ mol; ethylene, 0.42 MPa; 25 °C; 2 h. ^bDetermined by ¹H NMR. ^cDetermined by ¹³C NMR. ^dRatio of terminal olefins to internal olefins.

Table 34. Allylnickel Complexes Supported by Phosphine–Sulfonate Ligands



complex	R ¹	activity (10^3 g/mol _{Ni} ·h)	M_w	D_M	branches/1000C
71a ^a	Ph	8.9	2100	1.5	8
71b ^a	2-OMeC ₆ H ₄	6.8	3400	2.0	13
71a ^b	Ph	0.9	— ^d	— ^d	— ^d
71b ^b	2-OMeC ₆ H ₄	0.5	— ^d	— ^d	— ^d
71c ^b	Cy	1.5	— ^d	— ^d	— ^d
71d ^c		3400	624.0	2.3	— ^d

^aEthylene polymerization conditions: toluene, 2.5 mL; complex, 10 μ mol; ethylene, 3.0 MPa; 100 °C; 15 h. ^bNorbornene polymerization conditions: chlorobenzene, 10 mL; complex, 10 μ mol; norbornene, 1 g; 100 °C; 10 h. ^cNorbornene polymerization conditions: complex, 10 μ mol; 2 min. ^dNot reported.

Table 35. Ethylene Polymerization Using Phosphine–Sulfonate Neutral Nickel Catalysts in Different Solvents^a

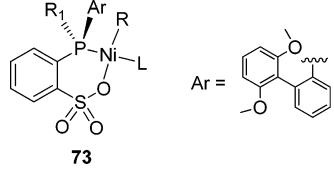
complex (μ mol)	solvent	temp (°C)	time (min)	activity (10^3 g PE/mol _{Ni} ·h)	M_n^b ($\times 10^3$)	branches/1000C
72a (5)	toluene	60	30	9800	0.8	15
72a (5)	CH ₃ C ₆ H ₁₁	60	30	5600	0.8	16
72a (10)	1-octene	50	135	364	>15	<1
72a (4)	heptane	90	60	61.6	>15	<1
72b (5)	toluene	90	30	3640	0.8	14
72b (4.5)	CH ₃ C ₆ H ₁₁	90	10	12600	0.8	15
72b (5)	1-octene	90	30	165.2	>15	<1
72b (8)	heptane	90	160	532	184 ^c	— ^d
72c (8)	heptane	90	60	476	0.7	18

^aPolymerization conditions: 250 mL steel reactor; ethylene, 4.0 MPa. ^bDetermined by ¹H NMR. ^cDetermined by GPC, referenced to linear PE.

^dNot determined.

stituted at the phosphorus atom, the attempts to synthesize PPh₃ stabilized phenyl nickel complex are not successful. The allyl complex 73a is thus synthesized instead, which is sluggish for ethylene polymerization giving moderate molecular weight polymer ($M_w = 1.4 \times 10^5$).¹⁷⁷ This may be a result of the low reactivity of allyl coordinated complex or the steric bulk of Ar substituents that prevent the access of the incoming ethylene

monomers. To address this issue, the authors design a novel ligand with one of the Ar moieties replaced by a less sterically demanding phenyl group. It is found that the corresponding allyl nickel complex 73b shows negligible activity toward ethylene under 90 °C, while phenyl nickel complex 73c stabilized by PPh₃ is highly active for ethylene polymerization (5.0×10^5 g PE/mol_{Ni}·h at 25 °C, 7.0×10^6 g PE/mol_{Ni}·h at 90

Table 36. High Molecular Weight PE Production by Phosphino–Arenesulfonate Nickel Complexes^a


complex	R ¹	R	L	temp (°C)	activity (10 ³ g/mol _{Ni} ·h)	M _w (×10 ³)	D _M	T _m
73a	Ar	η^3 -allyl		90	7.3	138.6	2.1	133.6
73b	Ph	η^3 -allyl		90				
73c	Ph	Ph	PPh ₃	25	515.2	753.6	1.9	136.1
73c ^b	Ph	Ph	PPh ₃	90	7028	22.5	2.3	118.1
73c ^c	Ph	Ph	PPh ₃	25	1010.8	831.6	1.9	136.9
73c ^d	Ph	Ph	PPh ₃	25	2676.8	40.4	6.7	127.1

^aPolymerization conditions: toluene, 80 mL; complexes 73a and 73b, 20 μmol, complex 73c 10 μmol; ethylene, 2.8 MPa; 1 h. ^b20 min. ^cWith 1.0 equiv of Ni(COD)₂. ^dWith 1.0 equiv of B(C₆F₅)₃, 20 min.

°C), affording high molecular weight polymer ($M_n = 7.5 \times 10^5$ at 25 °C). These results reveal that blocking only one of the transition metal faces is sufficient to inhibit associative displacement process, which may provide precious insight into the future design of late metal polymerization catalysts.¹⁷⁷

4.5. Carbene Nickel Catalysts

Waymouth et al. prepared two N-heterocyclic carbene (NHC) enolate nickel complexes 74a,b (Table 37).¹⁷⁸ As single-

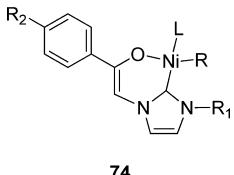
that by salicylaldimine³⁴ and diimine systems.⁸ However, further structure optimization is needed to improve their lifetime and tolerance toward polar monomers. The NHC enolate nickel allyl complexes 74c,d (Table 37) are also active ethylene polymerization catalysts in the presence of diethyl zinc (Et₂Zn), giving highly linear (branches <2 per 1000 carbon atoms) PE with low M_n (1300–2100) and broad molecular-weight dispersity. The authors believe that chain transfer to monomer and/or β-H elimination remains the dominant chain-transfer processes even in the presence of Et₂Zn.¹⁷⁹

The benzyl nickel complexes 75 and 76 bearing NHC ligands were synthesized and studied (Scheme 8).¹⁸⁰ Complexes 75a,b and 76a–d display poor activity for ethylene oligomerization, and slowly transform ethylene to butene. However, the imidazolinylidene η^3 -benzyl complexes 75a (4.1×10^4 g PNB/mol_{Ni}·h), 76a (2.1×10^4 g PNB/mol_{Ni}·h), and 76b (5.0×10^4 g PNB/mol_{Ni}·h) all exhibit good catalytic activities toward NBE polymerization without the addition of any activator. Among these catalysts, trifluoromethanesulfonato complex 76b shows the highest catalytic activity at room temperature. The improved activity (up to 3.3×10^5 g PNB/mol_{Ni}·h) at higher temperature (130 °C) suggests their good thermal stability.

5. BINUCLEAR NEUTRAL NICKEL CATALYSTS

In natural catalysts, such as some enzymes, two or more metal centers can be held together in close proximity. The position of the metal centers causes high local reagent concentrations, and conformationally advantageous substrate–active site proximity and interactions, resulting in superior activity or selectivity, which is known as cooperative effects.^{49,181,182} Inspired by these natural processes, the concept of cooperativity has been

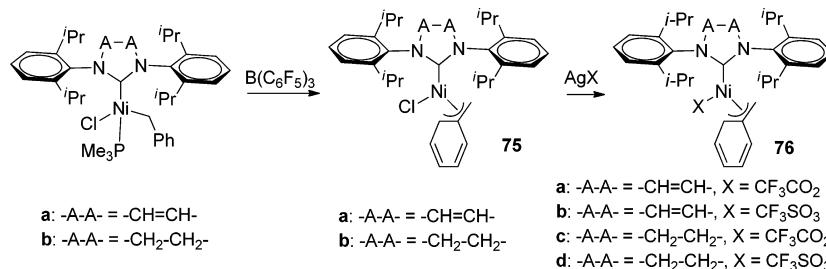
Table 37. N-Heterocyclic Carbene Enolates Nickel(II) Complexes



complex	R	L	R ¹	R ²
74a	Ph	PPh ₃	2,4,6-Me ₃ C ₆ H ₂	H
74b	Ph	PPh ₃	2,6-iPr ₂ C ₆ H ₃	H
74c	η^3 -allyl		2,6-iPr ₂ C ₆ H ₃	H
74d	η^3 -allyl		2,6-iPr ₂ C ₆ H ₃	NO ₂

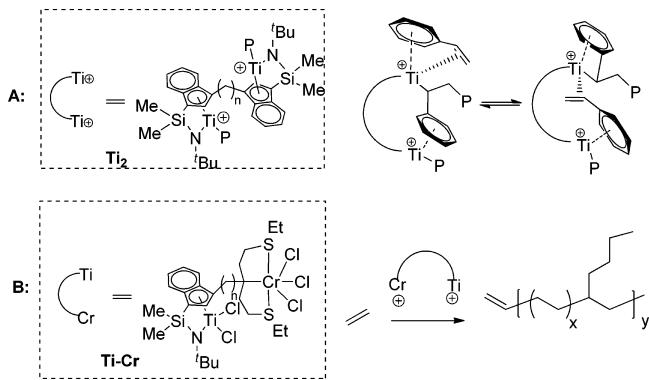
component catalysts, these complexes are active for ethylene and propylene polymerization to give linear PEs ($T_m = 123$ –132 °C) with modest M_n (1000–7100) and low molecular weight ($M_n = 540$) atactic propylene oligomers. End group analysis of the resultant PEs reveals a high selectivity for terminal α -olefins (95–98%). Catalytic activities for ethylene polymerization range from 0.8 to 56×10^3 g PE/mol_{Ni}·h, which are comparable to that by SHOP-type catalysts, but lower than

Scheme 8. Benzyl Nickel Complexes Bearing N-Heterocyclic Carbene Ligands



successfully applied to several other transformations,^{183–187} and cooperative effects involving binuclear olefin polymerization catalysts have been considered to give potentially excellent catalytic properties. In recent years, binuclear catalysts bearing early and late metals have been intensely studied, resulting in polymers with various unique structures and properties.⁴⁹ For example, CGC (constrained-geometry catalysts)-type titanium catalysts are sluggish for styrene polymerization due to the intramolecular deactivation by arene coordination to the metal center after styrene 2,1-insertion. However, the catalytic activity has been significantly improved by using binuclear CGC catalyst Ti₂. This result is due to the coordination of the last inserted styrene to the second metal center of binuclear CGC catalysts, which reduces the coordinative saturation at the polymerization site (Scheme 9A).¹⁸⁸ Heterobimetallic catalyst

Scheme 9. Cooperative Effects in Early Metal Olefin Polymerization Catalysts



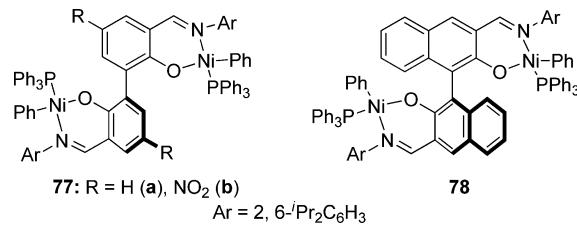
Ti–Cr contains an active ethylene trimerization chromium center, and a polymerization titanium center. In ethylene polymerization, this catalytic system can produce linear low-density polyethylenes (LLDPEs) with exclusive *n*-butyl branches. The branch density is significantly higher than that produced by a tandem mixture of corresponding titanium and chromium catalysts under identical conditions, indicating a possible concerted transfer of low molecular weight α -olefins generated at one metal center to the other (Scheme 9B).¹⁸⁹

As for neutral nickel catalysts, numerous skeletons have been designed and synthesized. Interactions between metal centers are thought to occur when the two metal centers are close enough in the process of homo- or copolymerization. Binuclear strategy has been applied into neutral nickel catalysts, aiming to explore the rationale of interactions between the metal centers and to conquer the difficulties faced in catalytic ethylene/polar monomer copolymerization. Binuclear neutral nickel catalysts, especially phenoxy–imine neutral nickel catalysts developed in recent years, are summarized in this section, and are classified according to the linkage between the two coordination units.

5.1. Phenoxy–Imine-Based Binuclear Catalysts

5.1.1. C-3 Bridges. For neutral nickel catalysts, especially phenoxy–imine systems, the presence of steric bulk in the ortho position of the phenoxy moiety (C-3 position) is a prerequisite for high catalytic efficiency. In this respect, binuclear catalysts that are linked through C-3 positions are promising designs. In 2005, Li et al. synthesized binuclear catalysts 77a,b starting from commercially available 2,2'-biphenol (Chart 16).¹⁹⁰ In these catalysts, two coordination units are linked together at the C-3 position, each of which acts

Chart 16. Binuclear Neutral Catalysts Reported by Li et al.



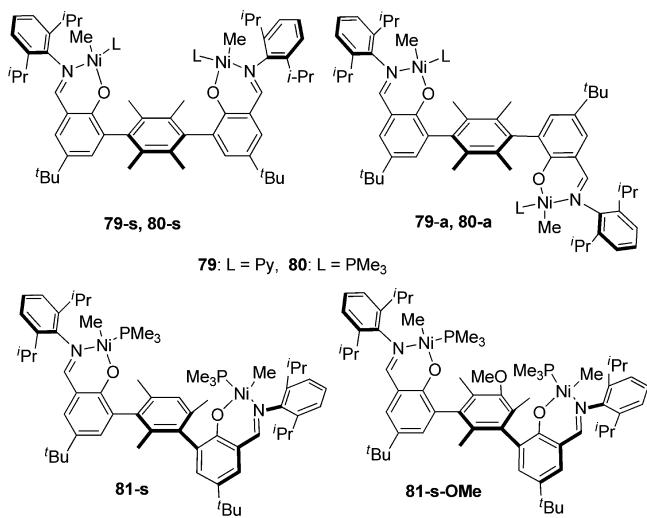
as the bulky substituent of the other unit. This presents a novel pathway to fulfill the mission of bulky substituents that otherwise requires time-consuming multiple synthetic procedures. As expected, the single component binuclear neutral nickel catalysts produce high molecular weight PE with good activity (4.55×10^5 g PE/mol_{Ni}·h), which remains high during the 120 min trial.¹⁹⁰ However, similar binuclear catalyst 78 derived from 1,1'-binaphthol only exhibits low activity for ethylene polymerization, indicating a possible blockage of ethylene monomer coordination or insertion by the too bulky ligand structure.

In combination with MMAO, binuclear complexes 77 and 78 are effective catalysts for vinyl-type polymerization of NBE.¹⁹¹ Complex 77a shows high activity up to 2.3×10^8 g PNB/mol_{Ni}·h, giving high M_w ($>10^6$) polymer products. Interestingly, despite the profound difference in the steric structures between 77 and 78, the observed catalytic activities are virtually identical. The size of the group at the ortho position of the phenoxy moiety appears to exhibit only limited influence on NBE polymerization activities, which is contrary to that for catalytic ethylene polymerizations.¹⁹¹

The single bond linkage in 77 only slightly restricts the relative rotation of the two coordination units, which reduces the possibility of their synergic work during polymerization. Atropisomers of terphenyl ligands appended with phenoxy and imine donors are formed by improving the steric bulk of the bridge. Agapie et al. designed a family of binuclear neutral nickel catalysts, which retain their conformations under polymerization conditions. While ethylene polymerization shows much resemblance between the mono- and dinuclear catalysts,¹⁹² their properties in the presence of additional amines are widely divergent. The *syn* bimetallic isomer 79-s shows less inhibition by added amines relative to the *anti* isomer 79-a, with the latter performing similarly to the corresponding mononuclear ones. The authors attribute the observed bimetallic effect to the close proximity of the two nickel centers, preventing the simultaneous block of the two metal centers by the amines. This hypothesis is supported by the fact that this effect is manifested when more bulky amines are added.¹⁹³

The atropisomers of dinuclear nickel bisphenoxyiminato catalysts 79-s and 79-a (Chart 17), and the corresponding mononuclear catalysts, are able to copolymerize ethylene with α -olefins in toluene or THF. PEs with methyl branches and longer side chains (three to six carbons depending on the α -olefins used) are produced.¹⁹² The *syn* catalyst 79-s is less active and generates lower molecular weight polymers than does the *anti* analogue 79-a, whereas more branching is observed using the *syn* catalyst (i.e., 31–49 branches per 1000 carbon atoms using 79-a and 54–92 branches per 1000 carbon atoms using 79-s). These observations can be attributed to the increased steric bulk.¹⁹² The steric consideration is also applied to the relative binding of ethylene and α -olefins when amines

Chart 17. Dinickel Complexes Based on Atropisomers of [N,O] Chelate Ligands



are coordinated. In the copolymerization of 1-hexene and ethylene in the presence of different amines, catalysts activated with Ni(COD)₂ afford copolymers with 0.2–1.3 mol % of 1-hexene incorporation. With amines, the incorporation of 1-hexene decreases, the trend of which is related to the distance between the two metal centers. Catalyst **81-s** exhibits the closest metal center distance, and, as expected, the decrease of incorporation of 1-hexene is the most obvious (from 1.1% to 0.2–0.3%). For **80-s**, however, this value slightly decreases from 1.2% to 0.8–1.0%. Notably, the Ni–Ni distance of the PMe₃ coordinated catalysts is significantly longer than those with pyridine ligands. This observation further supports the hypothesis that the steric repulsion can hinder the simultaneous binding of two amines. Introducing a –OMe group into the system (**81-s-OMe**) results in different levels of α -olefin incorporation and trend in catalytic activity.¹⁹⁴

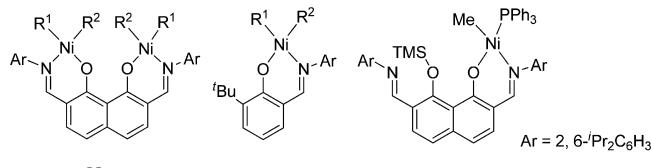
Copolymerization of ethylene with tertiary amino olefin (with ethyl or propyl substituents) is achieved by use of dinickel alkyl phenoxyiminato complexes **80-s**, **80-a**, **81-s**, and

81-s-OMe (Chart 17) in the presence of Ni(COD)₂, without masking of the polar heteroatom groups.¹⁹⁴ The *syn* complexes are more active than the *anti* analogues. More interestingly, the level of amino olefins incorporation is in the same range (0.1–0.8 mol %) as that for 1-hexene (0.2–1.3 mol %), and is not significantly affected by the number of –CH₂– units between the olefin and amine moieties. The Ni centers are likely too distant for a single monomer to coordinate to both, and varying the number of –CH₂– groups between the amine and olefin functionalities has no significant effect on the degree of polar monomer incorporation. A new mechanism different from previous proposals is thus suggested; that is, coordination of the amine moiety to Ni sterically hinders binding of an amine to the second Ni center for the *syn* complexes.¹⁹⁴ Ethylene or the olefin moiety of the polar comonomer has a lower steric profile than the amine and hence coordinates to the second Ni center, leading to the formation of a copolymer.¹⁹⁴

Although the relative movements are limited in 79–81, the distance between the two metal centers is too long. Marks et al. reported the use of binuclear neutral nickel catalysts 82a,b with rigid 2,7-diimino-1,8-dioxynaphthalene ligand to confine the two metal centers in close proximity. As a result, these catalysts show distinctly higher catalytic activities and higher methyl branching than the mononuclear ones.¹⁹⁵ Catalytic behaviors of the bimetallic complexes 82a,b (Table 38) in ethylene/NBE copolymerization are also investigated.¹⁹⁵ As compared to the monometallic 82-m-a, 82-m-b, and 82-m, complexes 82a,b exhibit higher activities and produce copolymers with more methyl branches (38 vs 11 methyl branches per 1000 carbon atoms). The molar percentage of NBE in the copolymers obtained by the bimetallic complexes (in the range from 9 to 11 mol %) is much higher than that by the monometallic counterparts (3 mol %).

On the basis of the aforementioned results, new dinuclear catalysts **82c,d** supported by rigid ligands with bulky *N*-aryl amine moieties⁶⁴ are designed to overcome the significant thermal deactivation due to the formation of bis-ligated complexes. The occurrence of $-\text{CF}_3$ moiety in **82d** results in the production of significantly higher molecular weight PE than **82c** substituted by CH_3 group (**82d**, $M_w = 2.5 \times 10^4$ vs **82c**, M_w

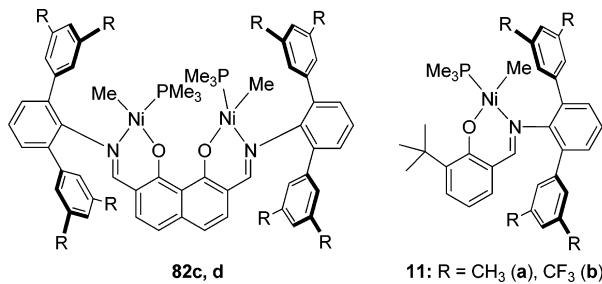
Table 38. Ethylene Polymerization and Ethylene/Norborne Copolymerization by Using Mono- and Bimetallic Neutral Nickel Catalysts^a



complex	R ¹	R ²	activity (10 ³ g/mol _{Ni} ·h)	82-m-a, 82-m-b		82-m-f		incorp.
				M _w ^b (×10 ³)	D _M	Me ^c branches		
82a	Me	PM ₃	49.7	10.3	2.6	80		
82b	PPh ₃	1-naphthyl	51.3	10.1	2.6	93		
82-m-a	1-naphthyl	PM ₃	25.2	11.7	2.5	52		
82-m-b	1-naphthyl	PPh ₃	25.9	10.5	2.5	54		
82-m			23.1	11.2	2.6	40		
82a ^b	Me	PM ₃	9.1	66.4	5.2	34		9
82b ^b	PPh ₃	1-naphthyl	8.4	65.8	4.5	38		11
82-m-a ^b	1-naphthyl	PM ₃	2.1	63.2	2.3	9		3
82-m-b ^b	1-naphthyl	PPh ₃	2.1	64.0	2.1	11		3

^aEthylene polymerization conditions: toluene, 25 mL; catalyst, 10 μmol ; 2 equiv of Ni(COD)₂; 25 °C; 40 min; ethylene, 0.7 MPa.

^bCopolymerization conditions: catalyst, 20 μmol ; 90 min; 225 equiv of norbornene.

Table 39. Ethylene/NBE (Co)polymerization by Binuclear Catalysts Bearing Bulky N-Aryl Amine Moieties in the Ligands^a

complex	R	activity (10^3 g/mol _{Ni} ·h)	M_w^b ($\times 10^3$)	D_M	Me ^c branches	incorp.
82c	Me	72	3.8	2.0	91	
82d	CF ₃	168	25	2.4	40	
11a ^b	Me	160	3.4	1.7	79	2.1
11b ^b	CF ₃	1200	68	2.9	21	<0.5
82c ^c	Me	4.8	4.5	2.2	93	7.0
82d ^c	CF ₃	4.8	16	2.8	44	3.0

^aEthylene polymerizations conditions: toluene, 50 mL; catalyst, 5 μmol; 2 equiv of Ni(COD)₂; ethylene, 0.8 MPa; 25 °C; 10 min.

^bCopolymerization conditions: 225 equiv of norbornene was added. ^cCopolymerization conditions: catalyst, 10 μmol; 225 equiv of norbornene; 40 min.

= 3.8×10^3), which is consistent with the result for 11a,b (Table 39).⁷⁹ Cooperative effects between the metal centers are observed in ethylene/NBE polymerizations, with bimetallic catalysts 82c and 82d enchaining 3- and 6-times more NBE than their monometallic counterparts 11a and 11b, respectively. The sterically encumbered binuclear catalysts 82c,d exhibit better thermal stability than the previously reported binuclear catalysts 82a,b. At 50 °C, however, both 82c and 82d gradually decompose with the reductive elimination from Ni–H groups to form free ligand and Ni(0) as the key step.

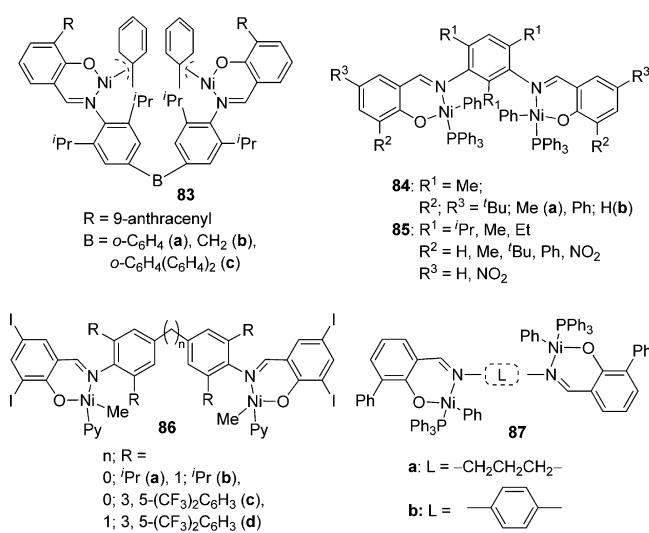
5.1.2. N-Aryl Moiety Bridges. A series of binuclear neutral nickel catalysts based on diamine-bridged salicylaldimine ligands have also been developed by different research groups. Complexes 83a–c (Chart 18) with various bridge units exhibit high catalytic activities toward ethylene polymerization that are comparable to the corresponding mononuclear catalyst $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-N=CH-(2-Anth-C}_6\text{H}_3\text{-O)-}\kappa^2\text{-[N,O]Ni}(\eta^3\text{-CH}_2\text{Ph})]$.¹⁹⁶ Catalyst 83b bearing a –CH₂– bridged ligand

displays the highest activity (up to 3×10^6 g PE/mol_{Ni}·h) among these binuclear ones. These bimetallic catalysts produce PE with more branches relative to the mononuclear counterparts probably due to a cooperative action between the two metal centers.¹⁹⁶ Bimetallic catalysts 83a–c with various linkages are able to copolymerize ethylene with polar norbornenes, such as 2-(methoxycarbonyl)norbornene and 2-(acetoxymethyl) norbornene.¹⁹⁶ Higher catalytic activity and incorporation of polar norbornene in the copolymers is observed versus the values using their mononuclear analogues. Bridge structure is found to greatly influence the incorporation of the comonomers, with C₆H₄–(C₆H₄)₂-bridged 83c exhibiting the highest polar comonomer incorporation. Cooperative effects between the two nickel centers are considered to be responsible for the copolymerization results. This is further supported by the geometry optimization performed with the Hartree–Fock theory.¹⁹⁶

m-Arene-bridged binuclear complexes 84a,b (Chart 18) are moderately active ethylene polymerization catalysts.¹⁹⁷ Complex 84b with a phenyl group at the R² position is more active than 84a with a *tert*-butyl group (1.2×10^5 vs 3.7×10^4 g PE/mol_{Ni}·h). This may be due to the additional electron-deficient nature of the phenyl group, similar to the electronic effect of mononuclear catalysts as reported by Grubbs et al.^{33,34} Huang et al. presented a systematic investigation on the *m*-arene-bridged binuclear neutral nickel complexes 85.¹⁹⁸ The catalytic activities are in the range from 2.0 to 31.4×10^4 g PE/mol_{Ni}·h in the presence or absence of the phosphine scavenger Ni(COD)₂. Highly branched PEs (46–127 branches per 1000 carbon atoms) with moderate molecular weights in a wide range of 10^4 to 10^6 are obtained. Electron-withdrawing groups on the ligand framework improve the catalytic activity and enhance the molecular weight of PE. Moreover, bimetallic catalysts exhibit much higher thermal stability and better polar functional group tolerance than the corresponding mononuclear analogues.

Ni(II) methylpyridine complexes 86a–d were synthesized by Mecking's group and served as effective single-component catalysts for ethylene polymerization.¹⁹⁹ Substitution in the 2,2',6,6'-position of the N-aryl moieties with 3,5-bis-

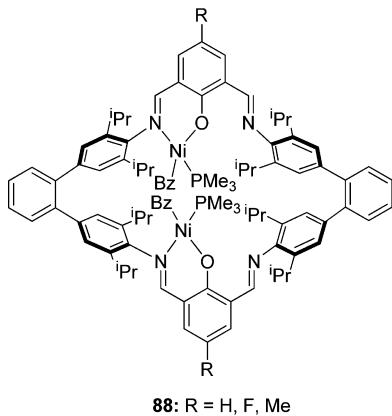
Chart 18. Binuclear Neutral Nickel Catalysts for Ethylene Polymerization



(trifluoromethyl)phenyl groups (**86c–d**) gives more active catalysts than the isopropyl-substituted **86a** and **86b**. The substantially higher catalytic activities of all binuclear complexes than those of the mononuclear catalysts suggest the existence of a bimetallic effect. The maximum catalytic activity as high as 9.5×10^6 g PE/mol_{Ni}·h is observed, giving rise to the PE with M_w up to 9.2×10^5 .¹⁹⁹ In contrast, no polymer is obtained by using *p*-arene-bridged **87a,b** as catalysts in the absence of a cocatalyst.²⁰⁰ Complex **87b** is inactive for ethylene polymerization even with the help of MAO. An activity of 3.8×10^5 g PE/mol_{Ni}·h is achieved by **87a** when Al/Ni ratio is 2000, yielding moderately branched (15 methyl branches per 1000 carbon atoms) PE with high M_w (up to 4.4×10^5) and moderate molecular-weight dispersity ($D_M = 2.2$).

5.1.3. Multiple Bridges. Macrocyclic neutral binuclear catalysts **88a–c** bearing both C-3 and N-aryl bridges exhibit satisfactory activities when combined with B(C₆F₅)₃ in hydrocarbon solvent (Chart 19).²⁰¹ These catalysts, however, are thermally unstable, showing negligible activity when the reaction temperature is elevated to 60 °C.

Chart 19. Dinuclear Nickel Catalysts Bearing Multiple Bridges



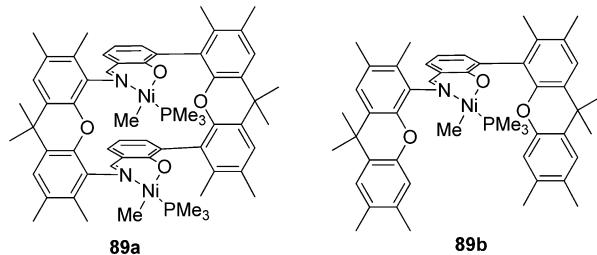
To realize the cooperative service in binuclear catalysts, double-decker-type binuclear nickel catalyst **89a** has been developed by Takeuchi and Osakada et al.²⁰² In their system, a

macrocyclic ligand poises the two nickel centers in close proximity (Ni–Ni distance 4.73 Å by X-ray crystallography). As for ethylene polymerization, **89a** was 5 times more active than the mononuclear **89b**, producing higher M_w (1.2×10^3 vs 1.7×10^3) PE with lower branches (59 vs 95 branches per 1000 carbon atoms) (Table 40). In the presence of 1,6-heptadiene or 1,7-octadiene, the **89a**/Ni(COD)₂ system copolymerizes them with ethylene, yielding copolymers containing –CH₂–C₅H₈–CH₂– groups, as well as pendant olefin for the latter case. In contrast, mononuclear catalyst **89b** gives only a small amount of polymer, in which no cyclic groups or pendant vinyl groups are observed. This unique property of the binuclear catalyst is ascribed to the stabilization of the intermediates, in which the pendant double bond coordinates to the other nickel center. Unfortunately, like other [N,O] mononuclear neutral nickel catalysts,²⁰³ binuclear catalyst **89a** is also unable to copolymerize olefin with fundamental polar monomers such as MA.

5.2. Other Binuclear Catalysts

Jin et al. reported binuclear neutral nickel catalysts **90a–d** based on 2,5-disubstituted amino-*p*-benzoquinone ligands. They produce high molecular weight branched PEs as single-component catalysts.²⁰⁴ The very broad molecular-weight dispersity ($D_M \approx 48.2$) indicates the presence of electronic communication between the two metal centers through the conjugated ligand structures. Binuclear acetylacetato (acac) complexes **91a–f** are moderately active toward ethylene when activated with AlEtCl₂, and are highly selective for the formation of C₄ and C₆ olefins (Chart 20).²⁰⁵ The selectivity toward 1-butene can be improved by using MAO as the cocatalyst at the expense of catalytic activity. Similar catalysts activated by MAO are also highly active (maximum activity: 6.64×10^7 g PNB/mol_{Ni}·h) for the addition polymerization of NBE, and the polymerization of MMA, giving syndiotactic-rich PMMA with broad molecular-weight dispersity. However, the possibility of radical mechanism can not be completely ruled out for MMA polymerization.²⁰⁶ Activated by MAO, binuclear complexes **91g–k** are capable of polymerizing styrene with the highest activity up to 7.46×10^5 g PS/mol_{Ni}·h (**91k**).²⁰⁷ The molecular weights of the resultant atactic polystyrenes range from (1.5 to 4.3) × 10⁴, which are significantly influenced by reaction temperature rather than substituents.

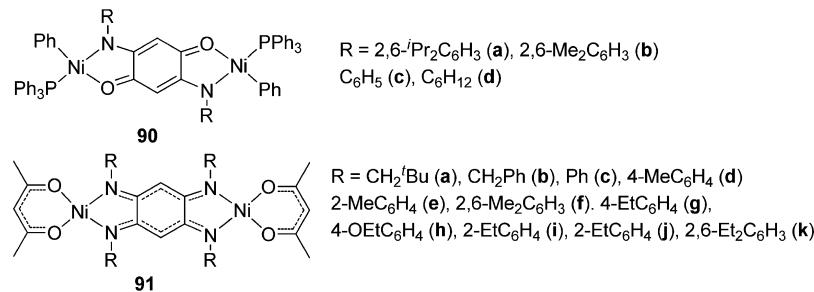
Table 40. Polymerization and Copolymerization of Ethylene by Binuclear and Mononuclear Salicylaldiminato Nickel Catalysts^a



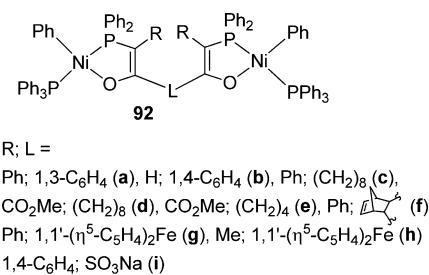
complex	comonomer	activity (10^3 g/mol _{Ni} ·h)	M_w ^b ($\times 10^3$)	D_M	branches/1000 C	incorp.
89a		10.5	12.0	4.5	59	
89b ^b		1.9	1.7	1.8	95	
89a	1,6-heptadiene	5.5	40.0	4.1	29	3.6
89a	1,7-octadiene	5.0	57.4	7.5	31	nd
89b ^b	1,7-octadiene	0.5	— ^c	— ^c	110	— ^c

^aPolymerizations conditions: toluene, 25 mL; complex, 20 μmol; Ni(COD)₂, 40 μmol; ethylene, 0.5 MPa; 225 equiv of comonomer; 25 °C; 90 min.

^bCatalyst, 20 μmol. ^cNot determined.

Chart 20. Binuclear Catalysts Based on Amino-*p*-benzoquinone and 2,5-Diamino-1,4-benzoquinonediimines Ligands

Kurtev and Tomov reported a series of $[\text{P},\text{O}]$ neutral nickel catalysts **92a–h** bearing bridges with different length and flexibility (Chart 21).²⁰⁸ As single-component catalysts, **92a,b,i**

Chart 21. Binuclear Phosphino–Enolate Nickel Catalysts with Various Bridges

are able to catalyze ethylene polymerization, and **92c,e,f** oligomerize ethylene to give less linear product than the corresponding mononuclear complexes, while **92g,h** are completely inactive.²⁰⁸ In the presence of various activators such as $\text{Ni}(\text{COD})_2$, all of the catalysts (**92a–i**) convert ethylene to polymers. Decreasing the distance between the metal centers results in an increase in catalytic productivity, which can be ascribed to the mutual influence of the active centers through indirect electronic interactions and stronger spatial repulsion. Catalyst **92f** with short distance between active centers and bigger steric bulk shows excellent catalytic activity. Notably, **92f** exhibits remarkable ability to polymerize ethylene in the presence of methanol and water–methanol mixtures.²⁰⁹ Catalysts **92a,e** are highly active for propylene dimerization when activated by Et_2AlCl . Kinetic studies using **92e** indicate that the reaction rate is first and second order with respect to the concentration of the catalyst and propylene, respectively.²¹⁰

Matt et al. also reported calixarene derived bis-ylidic complex **93a** in an attempt to confine two metal centers closely to each other (Chart 22).²¹¹ However, this binuclear catalyst is not very

active. The coordination of the proximate other phosphorus moiety to the metal center results in the formation of inactive compound **93b**. Other binuclear catalysts including those bridged at the $\text{Ni}-\text{C}$ moiety (**24**)¹¹⁷ and the N,N,N',N' -tetramethylethylenediamine (TMEDA) linked neutral nickel catalysts (**72a**)¹⁷⁶ have been introduced earlier in this Review, and thus will not be discussed here once again.

In conclusion, binuclear strategy in neutral nickel catalysts has received considerable attention in olefin homo- and copolymerization. Superior catalytic activity and selectivity have been achieved, giving polymers with novel structures. Binuclear catalysts are also found to tolerate polar reagents or monomers more than do their corresponding mononuclear analogues. However, successful copolymerization of olefin with commercial available polar monomers such as MA has not been reported using this strategy. Future research on binuclear catalysts should focus on further development of novel ligand structures or chelate modes, and better understanding of the mechanisms.

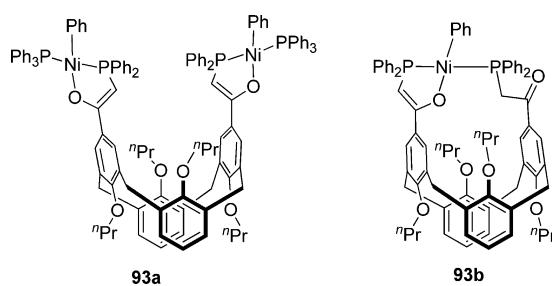
6. IN SITU GENERATED NEUTRAL NICKEL CATALYSTS

Most of the aforementioned neutral nickel catalysts feature a monoanionic ligand, a nickel–carbon bond, and a neutrally charged additional stabilizing ligand, which dominate reported neutral nickel olefin polymerization catalysts. However, other neutral systems without these evident characteristics also exist, which are classified herein as *in situ* neutral nickel catalysts.

The most notable example of *in situ* generated neutral nickel catalysts is SHOP catalysts developed for olefin oligomerization. A review published in 2007 has included most of the well-defined and *in situ* generated SHOP-type neutral nickel catalysts.³² Since then, only a limited number of *in situ* $[\text{P},\text{O}]$ neutral nickel catalysts have been reported. 2-Phosphinophenol ligands combined with $\text{Ni}(\text{COD})_2$ are used in the copolymerization of ethylene with α -olefins²¹² and alkyl-, aryl-, and ester-substituted α -olefins, yielding copolymer with isolated side groups.²¹³ In addition, the combination of salicylaldimine ligands with $\text{Ni}(\text{COD})_2$ gives active catalysts for the homopolymerization of ethylene,²¹⁴ MMA,¹⁹⁶ NBE,²¹⁵ and also the copolymerization of ethylene with MMA,²¹⁶ incorporating up to 6 mol % polar comonomer into the high molecular weight polymer chain. Apart from these typical *in situ* catalysts generated by free ligands and nickel source complexes such as $\text{Ni}(\text{COD})_2$, we introduce here some unconventional *in situ* nickel catalysts.

6.1. Bis-ligated Nickel Catalysts

SHOP-type and Grubbs-type neutral nickel catalysts, as disclosed in previous mechanism studies, tend to be deactivated in the process of polymerization to generate bis-ligated $[\text{P},\text{O}]$ or $[\text{N},\text{O}]$ nickel complexes that are inactive toward ethylene

Chart 22. Binuclear Catalyst Derived from Calixarene Skeleton and Its Deactivation Product

polymerization.^{34,96,97} The formation of bis-ligated complexes is considered to be an important deactivation pathway for neutral nickel catalysts, and strategies such as increasing the steric bulk have been introduced to prevent this process.²¹⁷ Notably, these bis-ligated complexes can be reactivated in the presence of activators such as MAO or $B(C_6F_5)_3$. Different from conventional neutral nickel catalysts, the generation of these latent active sites requires activators such as organoaluminum compounds, which prompts us to classify them as *in situ* catalysts.

6.1.1. Ethylene or Styrene Polymerization. Spectroscopic evidence reveals that monochelate methyl nickel products are generated when bis(salicylaldimine)nickel complexes are treated with MAO, and [alkyl(phosphino)-monosalicylaldiminate]nickel complexes are formed in the presence of phosphine ligands. Complexes **95a–d** and **96a** are active for ethylene oligomerization and generate minor amounts of polymeric products (Table 41).²¹⁸ Complex **96e**

Table 41. Bis-ligated Neutral Catalysts Reported for Ethylene or Styrene Polymerization

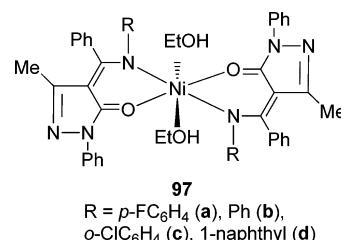
complex	X	Y	R	R'
95a	H	H	<i>i</i> Pr	
95b	H	OMe	<i>t</i> Bu	
95c	H	H	2,6- <i>i</i> PrC ₆ H ₁₁	
96a	H	H	<i>i</i> Pr	H
96b	Me	<i>t</i> Bu	<i>i</i> Pr	H
96c	NO ₂	NO ₂	H	H
96d	NO ₂	NO ₂	<i>i</i> Pr	H
96e	<i>t</i> Bu	Me	<i>i</i> Pr	H
96f	CH(Ph) ₂	CH(Ph) ₂	Me	H
96g	CH(Ph) ₂	CH(Ph) ₂	Et	H
96h	CH(Ph) ₂	CH(Ph) ₂	<i>i</i> Pr	H
96i	CH(Ph) ₂	CH(Ph) ₂	Me	Me
96j	CH(Ph) ₂	CH(Ph) ₂	Et	Me
96k	CH(Ph) ₂	CH(Ph) ₂	F	H

with more bulky 3- and 5-substituents can serve as a polymerization catalyst in THF with methyl lithium as activator.²¹⁹ Carlini et al. introduced bis-ligated complexes **96c,d** bearing electron-withdrawing nitro groups,²²⁰ and investigated their activity toward ethylene in the presence of MAO and other different organoaluminum activators under high ethylene pressure (5.0 MPa). These catalysts produce linear high molecular weight polymers in the presence of 5.0 equiv of Et₂AlCl, and give only oligomers under high Al/Ni ratio (Al/Ni = 15). They are completely inactive by use of less Lewis acidic AlEt₂OEt and *i*Bu₄Al₂O. This result represents the first example of bis(salicylaldimine)nickel complexes for ethylene polymerization giving linear high molecular weight PE in the presence of MAO. Moreover, higher molecular weight PE and higher catalytic activity can be achieved by supporting the catalysts to silica. The supporter silica acts as not

only an anchoring agent but also a scavenger of detrimental trimethyl aluminum (TMA).^{221–223}

Sun and Redshaw et al. found that phenoxy-imine bisligand nickel complexes (**96f–k**) bearing cumyl groups in the 3- and 5-positions exhibit good activity (2.89×10^6 g PE/mol_{Ni}·h) toward ethylene dimerization when combined with ethyl aluminum sesquichloride (EASC).²²⁴ In complexes **97a–d** (Chart 23), two ethanol solvent molecules coordinated and two

Chart 23. Bis(β -ketoamine)nickel Complexes Reported by Wu's Group



β -ketoamine ligands form a distorted octahedral nickel center (as determined by X-ray structural analysis).^{225,226} Activated by MAO, **97a** is very active for NBE polymerization (1.6×10^7 g PNB/mol_{Ni}·h), and **97b–d** polymerizes styrene to syndio-rich polymeric product with an activity up to 2.10×10^5 g polymer/mol_{Ni}·h.

6.1.2. Norbornene Polymerization. The most documented application of bis-ligated nickel complexes as polymerization catalysts has been related to NBE and its derivatives. Bis-ligated phenoxy-imine nickel complexes **98–100** catalyze NBE polymerization after treated with MAO (Chart 24).^{227,228} Among these catalysts, the one with substituted *N*-methyl moiety (**98**) yields high molecular weight (up to 3.3×10^6) amorphous PNB with an activity of 4.2×10^8 g PNB/mol_{Ni}·h.²²⁷ Nitro-substituted complexes are much more active than the analogues without electron-withdrawing groups. The steric

Chart 24. Bis-ligated Nickel Catalysts Bearing Phenoxy-Imine Ligands for NBE Polymerization

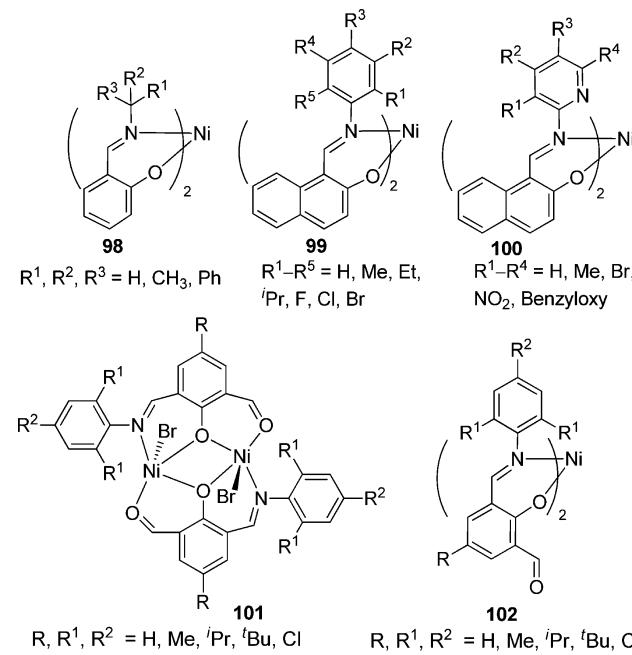
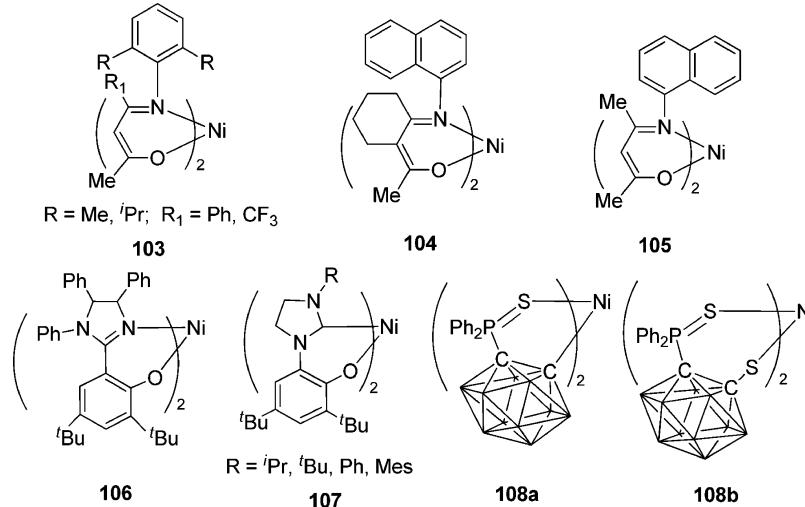


Chart 25. Bis-ligated Nickel Catalysts Based on Other Ligands for NBE Polymerization



bulk of the *N*-aryl group does not substantially affect the catalytic behavior and the characteristics of the resultant PNBS.²²⁹ The reaction of tridentate ligands with $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ affords bis-ligated complexes **101** and **102**, which show catalytic activities up to $9.88 \times 10^7 \text{ g PNB/mol}_{\text{Ni}} \cdot \text{h}$ in the presence of MAO.²³⁰

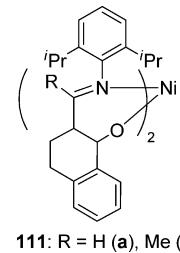
Apart from phenoxy-imine complexes, bis(β -ketoamino) nickel complexes **103–105** in combination with MAO or MMAO are also active for NBE polymerization.^{225,231–233} Moreover, some novel bis-ligated nickel complexes bearing phenoxy-imidazole (**106**),²³⁴ aryloxide-*N*-heterocyclic carbene (**107**),²³⁵ and carborane [S,C] or [S,S] (**108a,b**)²³⁶ ligands are also capable of polymerizing NBE (Chart 25).

6.1.3. Polar Monomer Polymerization. The aforementioned nitro-containing phenoxy-imine bis-ligated complexes **96c,d/MAO** are also active for MMA polymerization, while a blank experiment using sole bis-ligand nickel complexes or MAO yields no polymer at all.²²² High activity of up to $1.5 \times 10^5 \text{ g PMMA/mol}_{\text{Ni}} \cdot \text{h}$ is observed when the catalytic system is prepared under an ethylene atmosphere. Similar activity is also obtained using the less bulky catalyst, largely different from that observed by using the monochelate neutral nickel catalysts. Bis-ligated nickel complex **109** based on 8-hydroxy-quinoline derivative is able to promote MMA polymerization to give PMMA with characteristics significantly different from the corresponding radically prepared polymers,²³⁷ indicating a possible coordination-insertion mechanism (Chart 26). Wu et al. reported that bis(β -ketoamino) nickel complex **110/MAO** systems can polymerize MMA to give syndiotactic-rich polymer.²³⁸ On the basis of the microstructure analysis of the

polymer, however, a radical polymerization mechanism is favored.

6.1.4. Copolymerization. Considering that bis-ligated nickel complexes/MAO systems have been widely used in NBE polymerizations, the copolymerizations of NBE with its derivatives for the production of functionalized polymers are also tried. The bis(β -ketonaphthylamino)Ni(II)/B(C_6F_5)₃/AlEt₃ system copolymerizes NBE with NBA and NBM, incorporating beyond 50 mol % of the polar comonomer into the resultant noncrystalline copolymer.^{239,240} Moreover, NBE and its polar derivatives can be successfully copolymerized by using the **111/B(C_6F_5)₃** system without the help of organo-aluminum cocatalysts (Table 42). This avoids the unfavorable influence of residue aluminum on the performance of the polymeric product.^{129,170}

Because of the ease of synthesis and high stability, bis-ligated nickel complexes have been widely used for the (co)-polymerizations of olefin or polar monomers. However, the mechanisms of these (co)polymerization reactions are still ambiguous and require further investigation. The aluminum

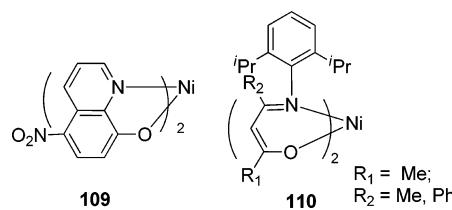
Table 42. Bis-ligated Nickel Catalysts Used for Copolymerization^a

complex	comonomer (mol %)	conversion (%)	M_w^b ($\times 10^3$)	D_M	incorp.	T_g ($^{\circ}\text{C}$)
111a	NBA (10)	62.0	48.8	1.9	6.3	355
111b^b	NBA (10)	56.8	279.0	2.3	5.8	278
111b^b	NBA (30)	33.9	247.0	2.3	10.3	275
111b^b	NBA (50)	14.4	180.0	1.9	12.0	264

^aPolymerization conditions: toluene, 20 mL; catalyst, 10 μmol ; 20 equiv of B(C_6F_5)₃; 1000 equiv of monomers; 50 $^{\circ}\text{C}$; 10 min.

^bToluene, 10 mL; catalyst, 5 μmol ; 2000 equiv of monomers; 60 $^{\circ}\text{C}$; 30 min.

Chart 26. Bis-ligated Nickel Catalysts Reported for Polar Monomer Polymerization

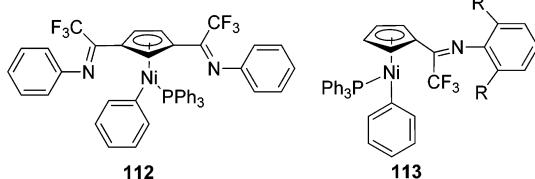


compounds used here often lead to the formation of radicals, or even initiate polymerizations themselves under certain reaction conditions, especially when polar monomers such as MMA are used as the (co)monomers.

6.2. Indenyl and Cyclopentadienyl Nickel Catalysts

In the presence of MAO, the phenylnickel phosphine compounds (**112** and **113**, Table 43) bearing iminoaryl-

Table 43. Cyclopentadienyl Nickel Complexes for Styrene Polymerization^a



complex	activity (10^5 g PS/mol _{Ni} ·h)	M_n ($\times 10^3$)	D_M	M_n
112	172.8	13.4	1.8	1400
113a	220.8	14.0	1.9	1500
113b	288.0	20.1	1.6	1200
113c	388.8	16.9	1.8	1300

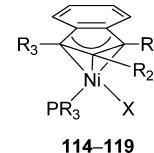
^aPolymerization conditions: toluene, 0.5 mL; catalyst, 0.25 μ mol; 1000 equiv of MAO; styrene, 3.0 mL; 50 °C; 10 min.

substituted cyclopentadienyl ligands exhibit high catalytic activities for styrene polymerization. Interestingly, polystyrenes produced by these catalysts have bimodal GPC traces corresponding to high molecular weight polymers ($M_n > 10^4$) with narrow distribution and low molecular weight oligomers ($M_n < 2 \times 10^3$). Under similar conditions, bulkier iminoaryl substitution is beneficial to catalytic activity enhancement (**113c** vs **113a,b**). The electron-withdrawing *N*-phenyl-2,2,2-trifluoroacetimidoyl groups may enhance the activity to some extent, but the effect is easily overridden by the negative influence of steric effects. The authors ascribe the higher catalytic activity of **113c**/MAO to its lower steric hindrance around the metal center, which allows easy access of the monomer to the active species. However, further investigations are still required to reveal the unambiguous and well-accepted polymerization mechanism for this system.²⁴¹

Similarly, a series of catalysts bearing indenyl ligands have been developed (Table 44).^{242–244} The nickel indenyl complexes Ind(PR₃)NiX (**114–115**, Ind = indenyl derivatives) dimerize and/or polymerize ethylene depending on the activators.²⁴² Activators such as AgBF₄, AlCl₃, and B(C₆F₅)₃ convert the Ni precursors to the highly electrophilic cations [IndNi(PR₃)]⁺, which lead to the exclusive formation of dimerization product 1-butenes. In contrast, both neutral species bearing a Ni(μ -Me)Al core (thought to be the active site for ethylene polymerization) and the cationic species (responsible for the dimerization) are formed when MAO is the activator. In this case, high molecular weight (around 10⁵) linear PE containing a small amount of ethyl branches (due to the insertion of 1-butene into the polymerization site) is obtained at a modest level of catalytic activity.

Shen et al. investigated the reactivity of this type of complexes toward styrene, and found that single-component **116** is inert toward the insertion of styrene, but the polymerization can be achieved in the presence of NaBPh₄ and PPh₃ to give the syndio-rich polystyrene with M_w around 10⁴. Unfortunately, the mechanistic details of styrene polymer-

Table 44. Nickel Catalysts Bearing Indenyl Ligands



complex	R	R^1	R^2	R^3	X
114a	Ph	Me	H	H	Cl
114b	Ph	Me	H	H	Me
114c	Ph	Me	H	H	CCPh
115a	Me	Me	H	H	Cl
115b	Cy	Me	H	H	Cl
115c	Ph	Me	H	Me	Cl
115d	Ph	Me	Me	H	Cl
115e	Ph	H	Ph	H	Cl
115f	Ph	Me	Ph	Me	Cl
115g	Ph	SiMe ₃	H	H	Cl
115h	Ph	iPr	H	H	Cl
116a	Ph	cyclopentyl	H	H	Cl
116b	Ph	benzyl	H	H	Cl
117	Ph	(CH ₂) ₂ N(CH ₃) ₂	H	H	Cl
118a	Ph	CH ₂ Py	H	H	Cl
118b	Ph	(CH ₂) ₂ NC ₄ H ₈	H	H	Cl
118c	Ph	(CH ₂) ₂ N'Pr ₂	H	H	Cl
119a	Ph	(CH ₂) ₂ CH=CH ₂	H	H	Cl
119b	Ph	Si(Me) ₂ CH ₂ CH=CH ₂	H	H	Cl

ization by these catalytic systems are not known with certainty.²⁴⁴ Bargarian et al. also introduced an amine group (**117**) to modify the property of this catalytic system.²⁴⁵ Cationic species [Ind(CH₂)₂NMe₂NiPPh₃]BPh₄ with the amino moiety coordinated to nickel is formed after chloride abstraction by NaBPh₄. This species is active for styrene polymerization and NBE oligomerization. Furthermore, the combination of **117** with MAO converts ethylene to butenes and linear PEs, whereas the addition of MAO or AlEt₃ to the aforementioned cationic species only leads to more efficient dimerization catalysis.²⁴³ These results indicate that the dimerization active species for this system is cationic, and the polymerization site is likely noncationic, similar to that observed for **114** and **115** (vide supra). Zargarian et al. devoted significant efforts in the modification of this system (cationic species generated by Cl⁻ abstraction), and found that the steric and electronic effects of both phosphine ligand²⁴⁶ and the aminoalkyl²⁴⁷ or olefin²⁴⁸ hemilabile groups (**118–119**) have significant influence on their polymerization characteristics.

6.3. Other In Situ Neutral Nickel Catalysts

Nickel complexes incorporating sulfonamide-imine ligands **120a–d** (Table 45) were synthesized and characterized, aiming to achieve a superior catalytic property by utilizing the interaction between the sulfonyl group and the metal center.²⁴⁹ Complexes **120a–c**/MAO show modest catalytic activity toward ethylene polymerization. **120b,c** give PEs with slightly higher molecular weights (M_w (1.5–1.7) $\times 10^5$) than catalyst **120a** ($M_w = 9.7 \times 10^4$). However, the binding of sulfonyl group prohibits ethylene coordination, leading to the inactivity of **120c** when no activator is added.

Jin's group reported the preparation of rare three-coordinate nickel(I) complexes **121** and **122** by the reaction of *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II) with bulky β -

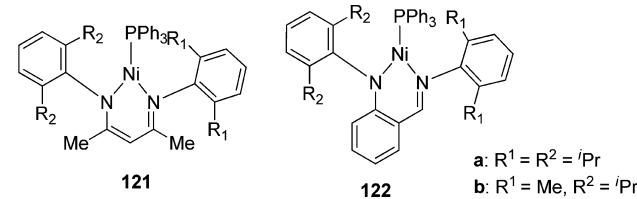
Table 45. Ethylene Polymerization by Nickel Complexes Based on Sulfonamide–Imine Ligands^a

complex	activity (10^3 g PE/mol _{Ni} ·h)	M_w ($\times 10^3$)	D_M
120a	77.0	97	2.4
120b	25.0	152	2.0
120c	58.0	169	2.1

^aPolymerization conditions: toluene, 30 mL; complex, 7 μ mol; 260 equiv of MAO; ethylene, 1.0 MPa; 40 °C; 30 min.

diketiminato ligands (Chart 27).^{91,250} While the complexes are not active toward ethylene polymerization with or without

Chart 27. Three Coordinated Nickel(I) Complexes Bearing Bulky Ligands



MAO, they show high activity (10^7 g PNB/mol_{Ni}·h) for the addition polymerization of NBE in the presence of MAO. High molecular weight polymers ($M_w \approx 10^6$) with relatively broad molecular-weight dispersities ($D_M = 2.6–7.0$) can be obtained by these catalytic systems.

7. POLYMERIZATION IN UNCONVENTIONAL MEDIA

7.1. Aqueous Polymerization

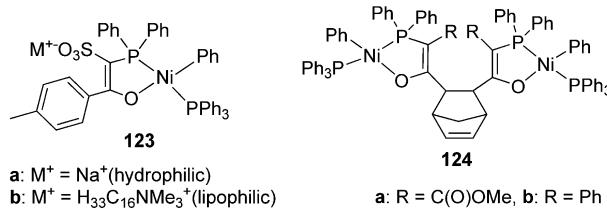
Polymer latices are widely used in industrial applications such as coating and paints, a key step of which is the evaporation of the dispersions.²⁵¹ In this respect, water is advantageous due to its environmentally benign character. On the other hand, using water as the reaction medium offers unique control of the heat of reaction. To date, polymer latices have been produced exclusively by free radical polymerization, which allows minor control over the polymer microstructures and the polymerizable monomers are also limited. Catalytic polymerization is attractive considering their unique property in the control over polymer microstructures and the polymer compositions. On the other hand, the range of polymerizable monomers for catalytic polymerization is complementary to that of free radical processes. Unfortunately, commercial coordination polymerization catalysts containing early transition metals are extremely oxophilic and reactive toward water, which hampers the development of catalytic aqueous polymerization.

Late metal catalysts are more tolerant toward polar media due to the less oxophilic nature, and catalysts reported in the recent years have exhibited their robustness against polar reagents. Neutral nickel catalysts pioneered by the seminal work of Keim et al. and Grubbs et al.^{33,34,94} are potential candidates in significant future applications. Values of catalytic aqueous

polymerization have attracted researchers to this field for both academic challenges and potential industrial applications. Mecking et al.,^{60,95,122,251–263} Claverie et al.,^{264,265} and others^{266,267} have been instrumental in this area during the past decade.

Phosphino–enolate neutral nickel catalysts are highly stable in alcoholic solvents. Polar solvents such as 1,4-butandiol can therefore be used as the reaction medium for easy separation of the resulting oligomer products. Similar catalysts are first tried in the aqueous polymerization process, and the parent catalyst is modified to be water-soluble by introducing $-\text{SO}_3^-\text{Na}$ moiety (123a, Chart 28).^{60,252} The catalytic productivity and the

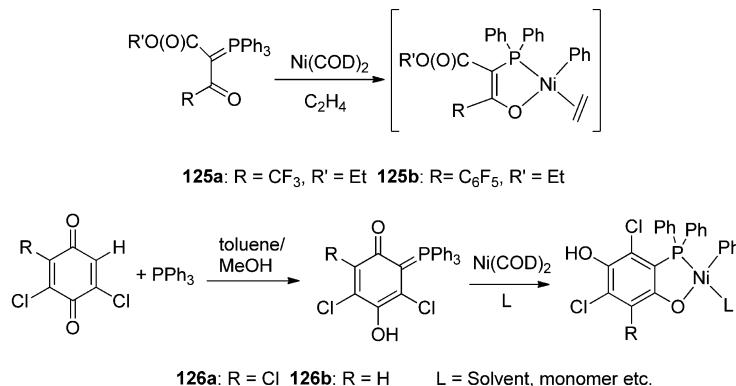
Chart 28. Phosphino–Enolate Neutral Nickel Catalysts Used in Aqueous Ethylene Polymerization



molecular weight of the polymeric products are both significantly decreased as compared to reactions run under identical conditions in organic solvents. This phenomenon is supposed to have resulted from the local low ethylene concentration in the aqueous medium rather than the irreversible deactivation of the catalysts, because the activity in aqueous polymerization remains for hours (as evidenced by polymerization runs for different reaction times). It has been found that ethylene concentration in neat acetone at 6 bar is similar to that in a 50:50 (v/v) water/acetone mixture at 50 bar. The fact that polymerization productivity and molecular weights are both similar in the two systems supports the aforementioned conclusion. The lipophilic complex 123b, which would be encapsulated in a small amount of organic phase during polymerization, behaves similarly to 123a in terms of polymer molecular weight and catalyst productivity. This result confirms the excellent stability of phosphino–enolate neutral nickel catalysts in water.

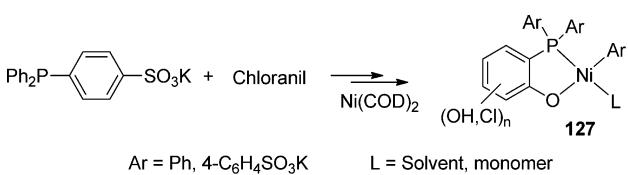
Emulsion polymerization carried out using 123a by the addition of anionic or neutral surfactants (SDS or Triton X-100) results in polymer latices of low molecular weight ($M_w = 3 \times 10^3$, $D_M = 2–3$) linear PE with the activity of 2.8×10^4 g PE/mol_{Ni}·h. The molecular weights of the polymers are similar to that in the aforementioned suspension-type polymerization. The polymer latices with particle sizes in the range of 80–300 nm are stable for a month or longer. Tomov et al. tried to use binuclear phosphino–enolate neutral nickel catalysts 124a,b to promote the emulsion polymerization of ethylene. The catalytic activity is 8.4×10^5 g PE/mol_{Ni}·h, but the resultant polymer latices are not stable.²⁶⁶

Claverie et al. reported ethylene miniemulsion polymerization using in situ generated neutral nickel catalysts (125a,b), and obtained stable polymer particles of sizes ranging from 100 to 500 nm in very high activity (4.8×10^6 g PE/mol_{Ni}·h).²⁶⁴ The concept of “miniemulsion polymerization” here is quite different from that in free radical polymerization. The new catalytic system consists of water, surfactant, a solution of the catalyst in a small amount of hydrocarbon solvent, and a hydrophobic agent (usually hexadecane). This mixture is

Scheme 10. In Situ Generated Neutral Nickel Catalysts for Aqueous Polymerizations

subjected to high shear to give a large amount of small droplets that disperse in the continuous liquid phase. In free radical miniemulsion polymerization, however, it is the monomer that is dispersed by ultrasound high shear, and the polymer particles are expected to be of the same size as that of the droplets. This is not applicable in catalytic polymerization because of the continuously fed gaseous ethylene monomer. Stable PE latices with 28% solid content are produced with the activity of 5.6×10^4 g PE/mol_{Ni}·h by Mecking et al. The in situ nickel catalysts (**126a,b**) used are generated from commercially available compounds, chlorinated derivatives of 1,4-benzoquinone, PPh₃, and Ni(COD)₂ (Scheme 10). The copolymerization of ethylene with 1-butene has also been realized using the same catalytic system.²⁵⁷ Miniemulsion polymerization allows the use of lipophilic catalysts without the need for modification to achieve water solubility, and renders the use of moderately stable catalysts in aqueous medium. However, there are still some limitations in this technique. The presence of hydrocarbon solvents is disadvantageous toward the formation of small polymer particles, because the lipophilic hydrocarbon phase needs to be dispersed by high shear, the degree of which may affect the eventual particle size. In fact, an aqueous solution of a hydrophilic catalyst represents the highest degree of dispersion, despite that the introduction of water-soluble moieties may require more synthetic efforts.

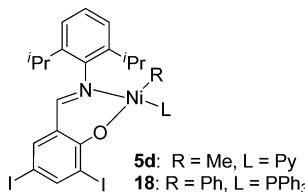
Mecking et al. have addressed this issue by using water-soluble catalysts (**127**, Scheme 11) generated *in situ* by the

Scheme 11. In Situ Hydrophilic Catalysts Used To Produce Extremely Small Polymer Particles

reaction of a stoichiometric amount of chloranil, potassium 4-(diphenylphosphino)benzenesulfonate (TPPMS), and Ni(COD)₂. The exposure of this catalytic system in an aqueous solution containing SDS to ethylene affords clear or only slightly turbid products with obvious ethylene consumption. This indicates the formation of latices containing extremely small particles (<20 nm by dynamic light scattering measurement) with sizes below visible light wavelength.^{259,268} Polymer dispersions with such small particles are not achievable using free radical polymerizations.

Despite the above-mentioned development in aqueous ethylene polymerization using [P,O] chelate neutral nickel catalysts, the polymer molecular weights are still low. The application of the polymer latices requires improvement in the molecular weight of the polymer material; thus polymerization using catalytic systems other than [P,O] chelate systems has also been explored.

Grubbs-type salicylaldiminato neutral nickel catalysts **5d** and **18** (vide supra) have been applied to aqueous ethylene polymerization (Chart 29).⁶⁰ As expected, this system shows a

Chart 29. [N,O] Nickel Catalysts Used To Produce High Molecular Weight PE Latices

lowered activity due to the low ethylene monomer concentration at the active centers in aqueous medium, and the catalysts' deactivation caused by the poison of water is also nonnegligible due to their moderately stable character. The resultant polymer M_n (>10⁴), however, is much higher than that by [P,O] nickel systems. This presents the first example of high molecular weight semicrystalline PE obtained in aqueous coordination polymerization.⁶⁰ Mecking et al. conducted the miniemulsion polymerization of ethylene using catalyst **5d** and produced high molecular weight (10⁵) PE aqueous latices for the first time by catalytic polymerization.²⁵⁴ The resultant polymer latices are stable for weeks or longer, and the average latex particle sizes are in the range of 90–350 nm as observed by light scattering measurement.

Mecking's group has made significant contributions in the area of emulsion polymerization by use of well-defined neutral nickel catalysts.^{60,76,258,261–263,269} The synthesis of PE dispersions in aqueous medium has been reported with lipophilic **8a** (Chart 5) and **128a** (Table 46), which are introduced to the reaction system as aqueous mini- or microemulsions of a solution in a small amount of toluene.^{76,258} Water-soluble catalysts can be synthesized via replacement of pyridine by highly water-soluble ligands L, where L = TPPTS [tri-(sodiumphenylsulfonate) phosphine] (**128e,g,i**), TPPDS [di-(sodiumphenylsulfonate)phenylphosphine] (**128f**), or H₂N-PEG [H₂N(CH₂CH₂O)_nMe (n = 52)] (**128h,j**).²⁶¹ These

Table 46. Neutral Nickel Catalysts for Emulsion Polymerization Developed by Mecking's Group

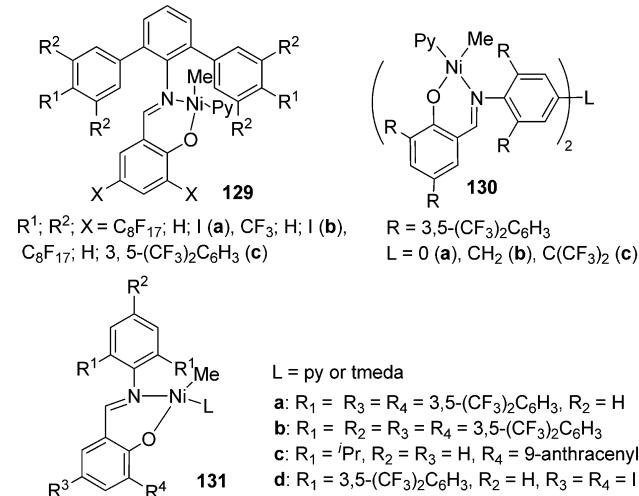
complex	X_1	X_2	L	R^1	R^2	R^3	ref			
								128l-n	128k	128o-r
8a	I	I	Py	CF ₃	H	CF ₃	76			
128a	I	I	TMEDA	CF ₃	H	CF ₃	259			
128b	I	I	TPPTS	CF ₃	H	CF ₃	261			
128c	I	I	TPPDS	CF ₃	H	CF ₃	261			
128d	I	I	H ₂ N-PEG	CF ₃	H	CF ₃	261			
128e	I	I	TPPTS	^t Bu	OH	^t Bu	261			
128f	I	I	TPPDS	^t Bu	OH	^t Bu	261			
128g	9-Ant	H	TPPTS	CF ₃	H	CF ₃	261			
128h	9-Ant	H	H ₂ N-PEG	CF ₃	H	CF ₃	261			
128i	9-Ant	H	TPPTS	^t Bu	OH	^t Bu	261			
128j	9-Ant	H	H ₂ N-PEG	^t Bu	OH	^t Bu	261			
128l	I	I	TPA	CF ₃	H	CF ₃	263			
128m	I	I	HETA	CF ₃	H	CF ₃	263			
128n	I	I	TEAPS	CF ₃	H	CF ₃	263			

catalysts are also used in aqueous emulsion polymerization and afford transparent high molecular weight PE dispersions in which extremely small polymer particles as low as 4–6 nm are obtained. The high activities of these catalysts are ascribed to the solvation effect of the hydrophilic ligands in water. Significantly, using the same catalytic system, single nanocrystals with a single crystalline lamella covered by thin amorphous layers have been formed in water, which can be confirmed by the combination of cryo-TEM and small-angle X-ray scattering methods. These nanocrystals are made of ca. 14 chains crystallized, which present as the smallest PE single crystals ever reported.²⁷⁰ Catalyst 128k bearing a fluorinated ligand and water-soluble additional stabilizing ligand TPPTS polymerizes ethylene into aqueous dispersions of strictly linear PE (<0.7 methyl branches per 1000 carbon atoms). In this process, highly ordered nanoscale crystals with ideal chain-folded structure are formed. The authors ascribe this phenomenon to the crystallization in the confinement of a nanoparticle and an ordered deposition of the growing polymer chain on the crystal growth front as the polymer chain is formed.²⁷¹ Further modification of the labile ligands L leads to complexes 128l–n with various solubilities in water. Emulsion polymerization of ethylene using these catalysts affords very different colloidal particles, implying that the size of PE particles is correlated to the degree of dispersion of the catalyst in the initial reaction mixture.²⁶³ Neutral nickel catalysts bearing enolato-imine ligands have also been modified to become water-soluble (128o–r). Aqueous polymerization using these catalysts produces high M_w (1.6×10^6) PE with very small particles (10–30 nm). By changing the catalyst structure and polymerization temperature, the branching degree (7–63 branches per 1000C) and consequently crystallinity ($\leq 25\text{--}50\%$) and T_m (75–129 °C) can be controlled in a wide range.²⁶⁹

7.2. Polymerization in scCO₂

Supercritical carbon dioxide (scCO₂) is an attractive reaction medium with three key features: (1) facile removal due to volatility at ambient conditions, (2) variation in solvent properties with density, and (3) environmental friendliness.^{272,273} Ethylene polymerization in scCO₂ using soluble neutral nickel complexes has been investigated by Leitner et al. and Mecking et al.^{273–276} Chart 30 illustrates the neutral nickel

Chart 30. Neutral Nickel Catalysts Used in scCO₂ for Ethylene Polymerization



catalysts (8a, 9k, and 129a–c) reported by Mecking et al., who designed fluorine-rich ligands to improve the CO₂-philic nature for polymerization in scCO₂. High molecular weight ($M_n \approx 10^4$) PEs with variable degrees of branching (predominantly methyl branches) are obtained in activities around 10⁴ g/mol_{Ni}·h. Complex 129c has the largest number of CO₂-philic groups but is the least active and produces polymers with the lowest molecular weight ($M_n < 10^4$), which is probably due to its low stability.²⁷⁴

The highly fluorinated binuclear nickel complexes 130a–c (Chart 30) supported by salicylaldimines bridged in para position of the N-aryl group have been applied to the ethylene polymerization in dense CO₂ and found to be single-component catalyst precursors.²⁷⁵ Semicrystalline PE with a moderate degree of branching (10–20 methyl branches per 1000 carbon atoms) and moderate molecular weight is obtained. Higher reaction temperature (70 °C) results in improved catalytic activities, but lower polymer molecular weight. The bridge moiety affects catalyst stability, but not the molecular weight and branching degree of the resulting PE. Strictly linear PE with ultra high molecular weight is obtained (<1 branch per 1000 carbon atoms, $M_w = 10^6$, $D_M = 1.8$) via appropriate choice of the catalyst precursor (131a-tmdea, Chart 30) and optimization of reaction conditions (CO₂ density, ethylene concentration, or temperature).²⁷⁶ 1-Hexene or NBE is incorporated into the PE main chain by use of 131a-tmdea as the catalyst in dense CO₂ at 50 °C. The T_m and crystallinity of the resulting copolymers can be controlled at lower than 70 °C and 20%, respectively, although the catalytic activities and polymer molecular weight are reduced as compared to the ethylene homopolymerization.

In summary, the two unconventional reaction media mentioned above are of great importance for olefin polymer-

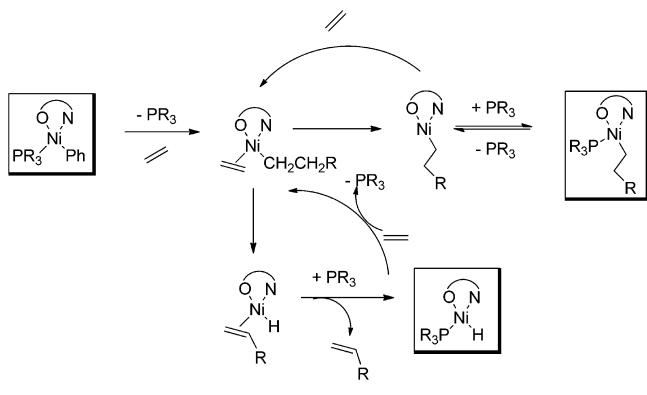
ization, allowing the access of polymers with various morphologies in controllable manner. As a family of robust, less oxophilic catalytic systems, neutral nickel catalysts are very promising with respect to this application. More efforts should be made in the future on the design and synthesis of new catalytic systems that are not only greatly tolerant toward the polar media but also as highly active as in conventional organic solvents.

8. CATALYTIC MECHANISM

8.1. Ethylene Polymerization Mechanism

Since the discovery of Brookhart's cationic nickel and palladium catalysts, considerable attention has been drawn to the mechanistic^{277–280} and theoretical^{281,282} investigations of diimine systems. In contrast, due to the relatively short history of neutral nickel polymerization catalysts, and the fact that neutral nickel complexes are less amenable to mechanistic investigations via direct NMR observations, mechanism studies on this unique catalyst system are scarce in the literature.²⁸³ As the first example, the highly efficient neutral nickel salicylaldiminato nickel complexes (**4a–f**, Chart 4) have been studied by Grubbs et al. using ¹H and ³¹P NMR,³⁴ in which three phosphine species (boxed structures in Scheme 12) can

Scheme 12. Possible Catalytic Cycle Based on ³¹P NMR Spectroscopic Studies



be observed. As described in the proposed catalytic cycle, ethylene polymerization is initiated by the leaving of the PR₃ ligand, followed by the repeated ethylene insertion (chain propagation). High M_w (>2.5 × 10⁵) and relatively linear PE (fewer than 10 branches per 1000 carbon atoms) is finally formed via the β-hydride elimination reaction. Meanwhile, this process is also accompanied by recoordination of PR₃ ligand with the active nickel center, leading to the formation of resting species, while the latter can be reinitiated by the removal of PR₃ ligand. This is in accordance with the experimental result that additional phosphine reduces the catalytic activity or

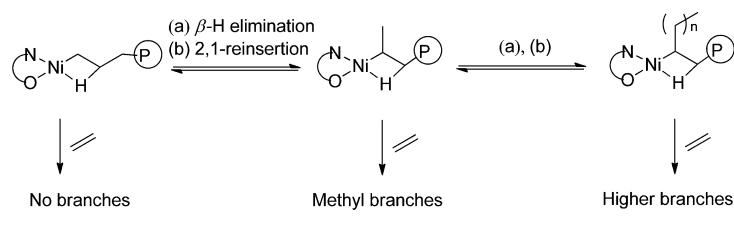
completely stops the polymerization. The aforementioned equilibrium reaction is influenced by structure of ligands and reaction conditions (e.g., reaction temperature).

Brookhart et al. have carried out extensive mechanistic investigations on ethylene polymerizations catalyzed by neutral nickel(II) catalysts derived from bulky anilinotropone ligands.^{106,107,284} For the [N,O]Ni(PPh₃) complexes, the catalyst resting state is an equilibrium mixture of [N,O]Ni(R)-(PPh₃) and [N,O]Ni(R)(C₂H₄) complexes. The catalytic activity is independent of ethylene concentration (saturation conditions) at high ethylene pressures, where the ethylene complex is strongly favored. The assumed mechanism for the formation of branched PE is presented in Scheme 13. Similar to that for the diimine nickel system,²⁰ a branch in polymer chain is first formed by β-hydride elimination of a growing polymer chain, followed by olefin rotation and reinsertion (chain walking) with opposite regiochemistry. This process may occur several times prior to ethylene insertion, leading to methyl as well as higher branches. As ethylene pressure increased, monomer coordination and insertion become more favorable, and therefore the PE with low branching content is formed. Conversely, when polymerization temperature is enhanced, the unimolecular branching pathway is increasingly favored over ethylene coordination and insertion, and, consequently, more branching can be introduced into the main chain. Chain walking has been considered as a characteristic feature of neutral nickel catalytic systems; low density branched polymers are easily obtained without additional α-olefin comonomers. Free ligand resulting from β-elimination of the nickel hydride complex can react with propagating nickel species to give inactive bis-ligated nickel complexes, which is reported to be the major catalyst decay pathway.

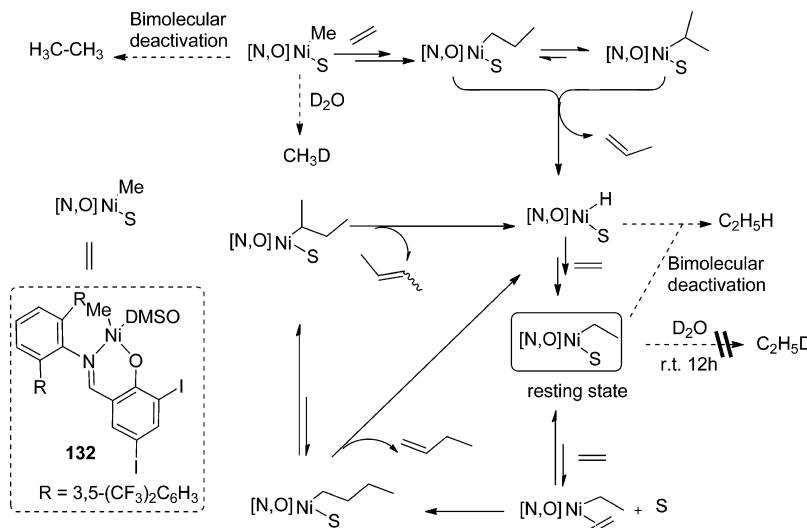
The dimethyl sulfoxide (DMSO) coordinated complex **132** is considered as a well-defined precursor that allows direct observation of the activation and deactivation of neutral nickel catalyst. The first comprehensive study of deactivation of this nickel catalyst, revealed by Mecking et al., is based on direct NMR spectroscopic observations during catalytic chain growth and quantitative kinetic studies of relevant intermediates (Scheme 14).²⁸⁵

According to their findings, D₂O does not significantly coordinate to the metal center or seriously hydrolyze the catalyst. In fact, only the Ni-Me moiety of the catalyst precursor is hydrolyzed by D₂O to form CH₃D. The hydrolysis of Ni(II)-alkyl species is a minor decomposition reaction as compared to the significant water-independent decomposition reactions, which is different from highly oxophilic early metal catalysts. Moreover, the main deactivation route of the nickel catalyst studied is the bimolecular elimination reaction between Ni(II)-alkyl species and Ni(II)-hydride [Ni(II)-R + Ni(II)-H → RH] and between two molecules of Ni(II)-Me catalyst

Scheme 13. Formation of Branched PE



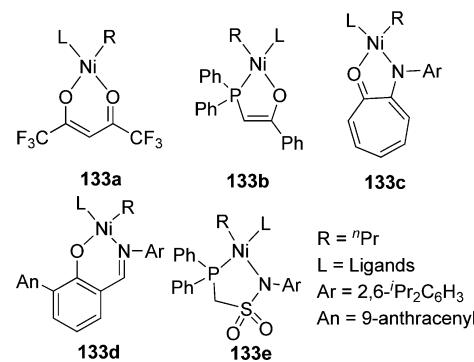
Scheme 14. Deactivation Pathways of Neutral Ni(II) Polymerization Catalysts



precursor species $[2\text{Ni}(\text{II})-\text{Me} \rightarrow \text{C}_2\text{H}_6]$ (Scheme 14). These results shed some light on the deactivation pathways of neutral nickel catalysts, which is valuable for the rational design of $[\text{N},\text{O}]$ as well as other nickel catalysts and for their application in aqueous polymerization.

Apart from the experimental methods used for the mechanism investigations, theoretical calculations are another powerful tool to study the elementary reactions (such as chain growth and chain termination) for neutral nickel catalysts.^{286–289} In two early works, Ziegler et al. studied the oligomerization mechanism of neutral nickel catalytic systems by means of DFT methods, and concluded that the major termination pathway is monomer-assisted β -hydrogen elimination rather than associate displacement.^{290,291} Density functional studies on salicylaldimine nickel polymerization catalysts with various substituents were also carried out by the same authors in 2009,²⁸⁹ in which both insertion and termination steps were examined. It is found that the β -hydrogen transfer (BHT) is the more favorable termination pathway than β -hydrogen elimination (BHE). The authors also confirmed the important role of electronic and steric effects on the performance of these catalysts. Tremendous efforts have been put into the research of chain termination reactions for different neutral nickel catalysts (used both for oligomerizations and for polymerizations) by DFT calculations in Jensen's group.^{286,287} A novel chain termination mechanism involving a pentacoordinate intermediate (without the dissociation of phosphine ligand) is proposed for neutral nickel catalysts, in which the alkyl chain rearranges to form a β -agostic species before β -hydrogen elimination and the dissociation of the olefinic chain. This new mechanism satisfactorily explains why SHOP-type catalyst **133b** produces oligomers and anilinotropone **133c** and Grubbs-type catalyst **133d** yield higher polymers.²⁸⁶ Recently, Jensen et al. further investigated the termination mechanisms for several catalysts (Chart 31) with different catalytic behavior (oligo- or polymerization, linear or branched products). DFT calculations display all of the most probable termination pathways, such as BHT and/or BHE for every catalyst. The Gibbs free energy difference $\Delta\Delta G^\ddagger$ between the barrier of propagation and termination calculated in this Review successfully reflects the tendency of the catalysts for oligo- or polymerization, which is in good agreement with the

Chart 31. Neutral Nickel Catalysts Used in DFT Calculations by Jensen's Group



experiment results. For example, the barrier difference for **133e** (a known oligomerization catalysts, see complex **62**, Chart 14) is 0.5 kcal/mol, indicative of similar propagation and termination rates. This means that the catalyst should oligomerize rather than polymerize ethylene. In addition, the investigation also reveals the different regiochemistry preferences for the β -hydrogen elimination process of the five neutral nickel catalysts, and the relationship between the donation capacity of the chelate atoms and β -hydrogen elimination.²⁸⁷ These results would no doubt be of great importance to the study of branching formation and be instructive for the future design of nickel catalysts. However, it should be noted that the accuracy of the methods used for computational studies in distinguishing between BHE versus BHT and in particular chain transfer versus chain propagation is not known for certain, despite that their results can satisfactorily explain the catalytic behavior of the catalysts studied here. The accuracy may be improved or confirmed by validating the computational model against experimental data (e.g., ΔG values), which are mostly hitherto unavailable.

8.2. Norbornene Polymerization Mechanism

Nickel complexes constitute a large group of highly active NBE polymerization catalysts with the activation of organoaluminum and/or borane cocatalysts.^{46,87} However, few studies have dealt with the catalytic mechanism, which results in a still ambiguous picture in certain aspects such as chain initiation and the effects

of ancillary ligands. Different from ethylene polymerization using nickel catalysts, the steric and electronic effects of the substituents tend to have negligible influence on the catalytic behavior of the catalysts (vide supra, section 2.2) with no apparent rationale. This phenomenon indicates a possible different mechanism from that of ethylene polymerization.

A prominent example of mechanistic studies came in 2003 by Goodall and Rhodes et al.²⁹² Complex 134a (Chart 32) bearing

Chart 32. Single-Component Fluorine-Containing Nickel Catalysts for NBE Polymerization



a neutral bidentate ligand and two electron-withdrawing $-C_6F_5$ groups serves as a single-component NBE polymerization catalyst. The activity of polymerization can be improved when the $[P,O]$ bidentate ligand is replaced by more labile η^6 -toluene (134b). This indicates that the bidentate ligand may have literally hampered the coordination of NBE monomer. This is completely different from nickel-catalyzed ethylene polymerizations, in which the bidentate ligands play a crucial role in catalysis.^{20,34} By analyzing the microstructure of the low molecular weight PNB obtained in the presence of ethylene, the authors suggest the insertion of NBE monomers into the $Ni-C_6F_5$ bonds (Scheme 15). After ethylene insertion and β -H elimination, a polymer chain forms with the two ends capped by $-C_6F_5$ and vinyl group, respectively. These results imply that a polymerization mechanism involving $-C_6F_5$ group transfer from boron to nickel likely occurs for NBE polymerizations catalyzed by bidentate nickel catalysts/ $B-(C_6F_5)_3$ systems. This has been further supported by the observation of the $-C_6F_5$ capped polymeric products in subsequent reports.¹²⁹ Moreover, complexes bearing other electron-withdrawing groups have also been reported to be viable for NBE polymerization (134c). Certainly, more studies are required to further elucidate the mechanism of NBE polymerization using nickel catalysts.

8.3. Polar Monomer Polymerization Mechanism

In the past decades, more attention has been focused on the copolymerization of α -olefins with polar monomers via coordination–insertion pathway by use of neutral nickel catalysts. To date, however, such copolymerization has suffered from either low efficiency or rapid catalyst deactivation, and an understanding of the problems associated with this reaction is

necessary and very important.^{203,293,294} Mecking et al. reported their comprehensive study results of the nature and reactivity of Ni(II) alkyl insertion products of methyl acrylate (MA) and vinyl acetate (VA) based on direct NMR spectroscopic observations.²⁰³ The observations of organometallic species and decomposition products originating from insertion of polar vinyl monomer into the key intermediates, Ni(II)–hydrides and Ni(II)–alkyls, of a neutral nickel complex (complex 135) provide the following insights:

(1) 2,1-Insertion of MA into the Ni(II)–H bond of complex 135 results in the formation of functionalized Ni(II) alkyl complex 135a (Scheme 16). Low-temperature 2D ROESY data demonstrate a weak Ni(II)…O=C β interaction of the oxygen atom of the carbonyl group with the Ni(II) center in 135a, which has also been confirmed by the gradient-corrected DFT ((BP86/LACPV*) level of theory.

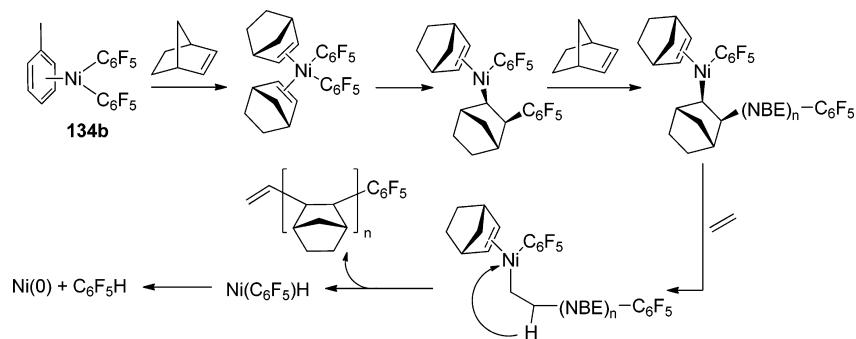
(2) Reaction of the Ni(II) hydride complex 135 with equal amount of ethylene and MA results in the formation of the insertion products of both monomers, 135a (the sum of 135a and its decomposition product methyl propanoate) and 135b (Scheme 17) in a 9:1 ratio. This indicates that MA and ethylene effectively compete with each other regarding the net outcome of coordination and insertion, which meets a prerequisite for effective catalytic copolymerization. Further insertions of MA or ethylene monomers are not observed, probably due to the low reactivity of the α -carbonyl-substituted metal alkyl for olefin polymerization.

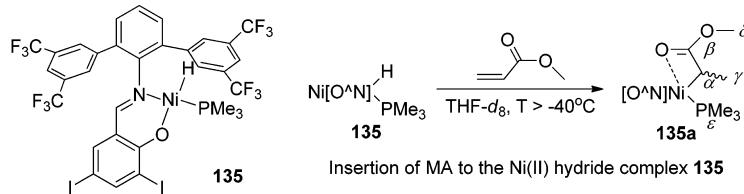
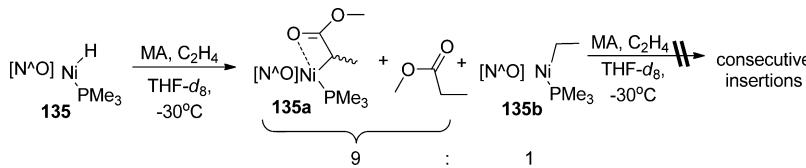
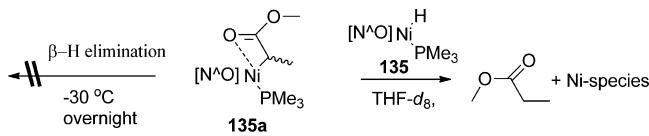
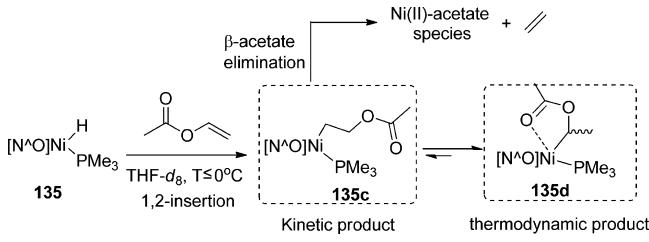
(3) At low temperature (at -40 °C), complex 135a readily reacts with Ni(II) hydride 135, which ultimately leads to catalyst decomposition, but is stable in the absence of the latter. At slightly higher temperature (0 °C), however, β -H elimination of 135a itself occurs to form Ni(II) hydride 135, which can decompose complex 135a via bimolecular reaction (Scheme 18).

(4) While the analogous Ni(II)–Et species is practically stable toward hydrolysis at 55 °C, the α -carbonyl-substituted metal alkyl originating from 2,1-insertion of MA into higher Ni(II) alkyls is subject to rapid hydrolysis at room temperature. This indicates that hydrolysis is also a major decomposition pathway for the ethylene/polar monomer copolymerization.

(5) The insertion of VA into the Ni(II)–hydride bond of 135 is more difficult as compared to that of MA. Insertion takes place at about 0 °C to give the kinetic 1,2-insertion product 135c, which rearranges into the thermodynamically favored 2,1-insertion product 135d (Scheme 19). Decomposition of 135c by β -acetate elimination occurs even at low temperatures to give Ni(II)–acetate species and ethylene.

Scheme 15. NBE Polymerization Mechanism in the Presence of Ethylene



Scheme 16. Insertion of MA into the Ni(II) Hydride Complex 135**Scheme 17.** Competitive Reaction of MA and Ethylene with 135**Scheme 18.** Bimolecular Decomposition of 135a in the Presence of Ni(II) Hydride Species 135**Scheme 19.** Insertion of VA into Ni(II) Hydride Species 135

(6) Unlike MA, VA does not insert into the nickel–carbon bond of the higher Ni(II) alkyl species 135e at room temperature but reacts with Ni(II) hydride species in equilibrium with 135e to yield 135f. Rapid β -elimination from 135f gives ethylene and Ni(II)–acetate species (Scheme 20).

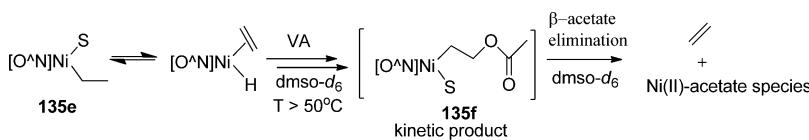
As compared to MA, another readily available polar monomer MMA has been less investigated in the literature for insertion copolymerizations. Most of the aforementioned homo- and copolymerizations of MMA by using neutral nickel catalysts require organoaluminum compounds as a cocatalyst, which makes it impossible to completely rule out the possibility of radical mechanisms (vide supra), even when radical traps are used in some cases. One exception is Gibson's work using phosphino–enolate neutral nickel catalysts, which performed as single-component catalysts or were generated *in situ*.¹⁶⁶ The insertion of MMA monomer followed by immediate β -H elimination provides functionalized PE with unsaturated ester end groups. Other attempts have also been reported using

neutral nickel catalysts based on phosphine–sulfonate¹⁷¹ and salicylaldimine ligands,¹⁹⁸ in which ethylene homopolymer rather than copolymer is obtained in the presence of MMA. Neutral nickel catalysts generated *in situ* by $\text{Ni}(\text{COD})_2$ and phosphino–phenolate ligands are even completely poisoned by MMA.²¹³ As a matter of fact, even the versatile phosphine–sulfonate neutral palladium catalysts, which proved to be compatible with a broad scope of polar vinyl monomers, are not able to incorporate MMA to the polymer chain, although the 1,2- or 2,1-insertion of MMA does occur.²⁹⁵

Generally, neutral nickel catalysts^{166,296–298} are to date less successful as compared to phosphine–sulfonate palladium catalysts for the copolymerization of olefin with these readily available polar comonomers such as MA and VA. However, considering the more variable catalyst frameworks and more controllable polymer microstructures produced by neutral nickel catalysts, as well as their less expensive nature, copolymerizations using neutral nickel catalysts are still attractive. The above investigations shed light on the reaction and deactivation pathways using $[\text{N}^{\text{O}}]$ neutral nickel catalysts, and expose several key problems that existed in the copolymerization reactions, such as the low reactivity of the α -carbonyl-substituted metal alkyl bond and the bimolecular deactivation reaction. This will be helpful for future investigation on neutral nickel catalysts.

9. CONCLUSION AND OUTLOOK

As described above, great progress in the area of neutral nickel catalysts for olefin homo- and copolymerization has been achieved in the past decade. As compared to the traditional early metal catalysts, neutral nickel catalysts show some unique advantages such as functional group tolerance, facile initiation, and controllable branching structure of the polymeric product. Oligomers, linear to highly branched polymers, as well as copolymers containing polar functionalities can be obtained using these catalysts under moderate reaction conditions. The microstructures of the polymeric products can be readily

Scheme 20. Reactivity of VA toward Higher Ni(II) Alkyl Species

controlled by adjusting the structure of the ligands or/and reaction conditions (temperature, solvents, ethylene pressure, etc.).

As a family of late metal catalysts with neutrally charged active sites, their potential application would definitely be related to the functional group tolerance and polar monomer copolymerization. Accordingly, catalytic (co)polymerizations in scCO₂ and in aqueous media ([section 7](#)) have been achieved using neutral nickel catalysts, and polar norbornene derivatives and vinyl monomers that bear functional groups remote to the olefinic double bond have been successfully copolymerized ([sections 2.3](#) and [3.3](#)) by using this family of catalysts. On the basis of the mechanistic understanding of olefin/polar monomers copolymerization and all of the effort devoted to this area, it is reasonable to believe that incorporation of commercially available polar monomers such as MA and VA is attainable by rational design of catalyst structures. To achieve this attractive and yet challenging goal using inexpensive nickel catalysts via coordination–insertion polymerization would no doubt be of great industrial interest. Furthermore, with the advent of efficient binuclear catalysts and phosphine–sulfonate palladium catalysts, some useful concepts have been introduced to nickel systems, leading to unique catalyst properties and new polymer structures. Given all of these developments in fundamental aspects and in the immobilization of homogeneous olefin polymerization catalysts, which is crucial to preventing reactor fouling and facilitating continuous operations in industrial gas-phase and slurry processes,^{298–301} we believe that the practical use of these less expensive and highly active catalysts is rather promising.

On the basis of the results presented in this Review, further efforts concerning homogeneous neutral nickel catalysts are still needed to address the following challenges:

(1) Improvement of the catalytic activities for ethylene/polar monomers copolymerization and the molecular weight of the resultant copolymer. To this end, designing new catalytic systems based on the previously established rationales may be required.

(2) Broaden the scope of the variety of polar monomers suitable for the copolymerization catalyzed by neutral nickel catalysts. It is desirable that more polar monomers, especially those abundant and less expensive ones, can be incorporated into the polyolefin main chain to give novel copolymers with unique physical and chemical properties.

(3) Identification of the physical and chemical properties of the obtained polymeric materials. With the advent of new nickel catalysts, the properties and potential applications of the polymers require extensive investigation because the potential performance of them has not yet been completely revealed.

(4) Regio- or stereoselective polymerization of polar vinyl monomers or α -olefins and their copolymerizations. These (co)polymerization reactions remain a big challenge to date not only for neutral nickel catalysts, but for the other late metal catalysts, and should be a hot topic in the near future.

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Notes

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Li Pan was born in Qingdao, China, in 1978. She received her B.S. (2001) from Qingdao University and Ph.D. (2007) in organic chemistry from Changchun Institute of Applied Chemistry (Changchun, China) under the direction of Prof. Yuesheng Li, and worked as an assistant professor in the same group from 2007 to 2009 on the transition-metal-catalyzed olefin (co)polymerization, polyolefin functionalization, and physical performance. She joined Prof. Zhaomin Hou's group at The Institute of Physical and Chemical Research, Japan (RIKEN, 2009–2012), and Prof. Douglas W. Stephan's group at University of Toronto, Canada (2013–2014), as a Postdoctoral Fellow. She is currently a professor at Tianjin University, focusing her research on the synthesis of novel high performance polymers.



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GLOSSARY

CGC	constrained-geometry catalyst
DFT	density functional theory
EASC	ethyl aluminum sesquichloride
HDPE	high-density polyethylene

LLDPE	linear low-density polyethylene
MA	methyl acrylate
MAO	methylaluminoxane
MMA	methyl methacrylate
MMAO	modified methylaluminoxane
M_n	number-average molecular weight
M_w	weight-average molecular weight
NBE	norbornene
NBA	5-norbornene-2-yl acetate
NBM	5-norbornene-2-yl-methanol
NBO	5-norbornene-2-ol
Ni(COD) ₂	bis(1,5-cyclooctadiene)nickel
PE	polyethylene
PNB	polynorbornene
PS	polystyrene
Py	pyridine
SDS	sodium dodecyl sulfate
SHOP	Shell Higher Olefin Process
T_g	glass transition temperature
T_m	melting temperature
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TPPDS	di(sodiumphenylsulfonate)-phenylphosphine
TPPTS	tri(sodiumphenylsulfonate) phosphine
UHMWPE	ultrahigh-molecular-weight polyethylene

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