

Chapter 2

Late-Transition Metal Complexes with Mixed N^O, N^S, N^P Chelating Ligands for Olefin Polymerization Catalysis

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Abstract Mixed chelating ligands which contain a nitrogen donor atom in combination with P, O, or S are a novel class of frameworks for generating complexes of unusual reactivity. Complexes of group X metals (Ni and Pd) supported by these ligands are currently exploited as homogeneous catalysts for: olefin polymerization, copolymerization of olefins with functionalized monomers, olefin polymerization in uncommon solvent such as water. This chapter covers the literature on the subject.

2.1 Introduction

Polyolefins, namely produced by heterogenous early transition metal catalysts, are a multibillion dollar a year industry [1]. It has been more than half a century since polyethylene's commercialization, still enormous progresses have been made in the past 30 years in the polymerization with homogeneous and well defined catalysts, which lead to well controlled polymer architectures and to novel materials [2–6]. Despite these successes, the controlled copolymerization of simple olefins with polar functional monomers via the coordination–insertion mechanism has remained a challenge in the polyolefin field [7, 8]. The high oxophilicity of early transition metal catalysts (titanium, zirconium, or chromium) causes them to be poisoned by polar comonomers. Thus, great interest in late transition metal catalysts arises from their tolerance to polar molecules, which can lead to the

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copolymerization of polar vinyl monomers with non polar olefins and the copolymerization of olefins with carbon monoxide [9–13].

In the mid-1990s the first example of copolymerization of ethylene with methacrylate by cationic Pd(II) α -diimine complexes was reported by Brookhart [14–20]. This constituted a major breakthrough that generated a great interest in this field. Now, organometallic complexes of group X metals (Ni and Pd) used as catalyst precursors in homogeneous olefin (co)polymerization are conventionally supported by nitrogen containing chelating ligands. Noteworthy are the cationic Ni- and Pd-based diimine catalysts which serve as catalysts for the polymerization of ethylene and α -olefins to high molar mass materials, with turnover frequencies (TOFs) as high as those of traditional homogeneous metallocene catalysts based on early transition metals. The key features of these systems are: (1) the highly electrophilic and cationic Ni and Pd metal centers; (2) the use of sterically encumbered diimine ligands; (3) the use of noncoordinating counterions or the use of reagents thought to produce non-coordinating counterions. Nevertheless and exactly for the same features α -diimine Ni and Pd catalysts suffer from some shortcomings in copolymerization of α -olefins with polar vinyl monomers. The cationic nature of metal center favours the coordination of polar vinyl monomers by polar functional group rather than by double bond. In addition, activators such as AlR_3 or methylaluminoxane (MAO) can react with the polar vinyl comonomers, leading to protected and high encumbered species or starting their homopolymerization by other mechanisms than coordination polymerization [21]. A relevant review appeared describing late transition metal catalysts containing N–N ligands [9].

Neutral hydrocarbyl Ni and Pd active species, which bear anionic chelating ancillary ligands, are proving to be the effective candidates for copolymerization reactions of olefins with polar vinyl monomers for both electronic and structural reasons which result in high functional group tolerance and easy activation. Attempts to introduce negative charge in N–N ligands resulted in poor activity and prompted the interest in the mixed ligand concept. Mixed ligands which have different chemical donor functions, such as hard and soft donor atoms or groups, find increasing use in chemistry, mainly because they often exhibit a hemilabile character in the coordination sphere of a metal complex. First and successfully applied in olefin oligomerization the mixed ligand concept is the base of Shell higher olefin process (SHOP) which exploits Ni and Pd complexes with anionic P–O ligands to produce linear olefins (C_6 – C_{20}) [22–24].

Herein, we focus on nitrogen containing mixed ligands as building blocks of catalysts for olefin polymerization. We particularly focus on some notable developments on mixed N–O, N–P, and N–S supporting ligands and their uses in late transition-metal-catalyzed polymerization. Thus, this review covers families of catalysts based on mixed chelating ligands, containing nitrogen, that are active for the homopolymerization of ethylene and the copolymerization of ethylene with α -olefins and polar comonomers. Late metal catalysts not active for ethylene polymerization are not included. Catalyst syntheses, activities, and chain-growth mechanisms and the influence of these factors on the structures of the resulting polymers are discussed.

2.2 Mixed Ligand Concept

Mixed ligands are bi- or polydentate ligands that contain at least two different types of chemical functionality capable of binding to metal centers. There is an increasing interest in the development of these ligands, as the different features associated with each donor atom confer unique reactivity to their metal complexes [25–32]. In homogeneous catalysis these functionalities are often chosen to be very different from each other to increase the differentiation between their interactions with the metal center(s). In turn, these functionalities will influence the bonding/reactivity of the other ligands bound to the metal. Ligands containing both hard and soft donors have often been synthesized, the hope being that different and contrasting reactivity associated within the same molecule would lead to novel and unprecedented properties for the resulting metal complexes.

The greater the σ -donor ability is, the greater the π -acceptor (π -back donation from metal to ligand) capacity is in the metal complexes and thus hard in the HSAB Pearson's scale [33]. When coordinated to transition metal ions, N-ligands are generally strong σ -donors, while the π -character depends on the frameworks. Also oxygen ligands are hard while P- and S-ligands are soft. The sulfur donor ligands, which are poor σ -donor and poor π -acceptor ligands, are the softest. Phosphine ligands are generally regarded as σ -donors and π -acceptors. Mixed N–O, N–P, or N–S ligands can display quite different coordination modes compared to N–N ligands. Of particular interest is that modification of the steric and electronic properties of either the phosphine or the nitrogen donor function is expected to influence the coordination chemistry and catalysis with these systems.

Over the past 15 years, much effort has been dedicated to the development of mixed donor ligands for Ni and Pd complexes as olefin polymerization catalysts [6–10]. This class of ligands is particularly interesting because of the different *trans*-effect, as a result of different donor and acceptor properties of the two coordinating groups in the ligand. The differences of these donor atoms would offer an effective tool in targeting particular catalytic activity and comonomer discrimination even though the influence of a ligand on catalytic properties of a transition metal complex is still hard to predict. For example, complexes with P–N ligands can have the advantage of improved thermal stability in catalysis with respect to those with N–N ligands, as nickel complexes with P–N ligands showed much higher thermal stability than related diimine complexes [34, 35]. This might overcome the problem of fast catalyst deactivation at high temperatures that diimine-based catalysts suffer [36]. Alternating the donor atom on the ligand scaffold to adjust the catalyst activity, selectivity, and reactivity towards different monomers can play an important role in achieving polymers with high molar masses and novel architectures. This kind of versatility is of interest both in basic research and for catalytic applications.

Nickel and palladium complexes with mixed ligands have been used in the oligomerization [37] and polymerization of ethylene [9–11]. We will limit ourselves to the presentation of ligands which form complexes that after activation

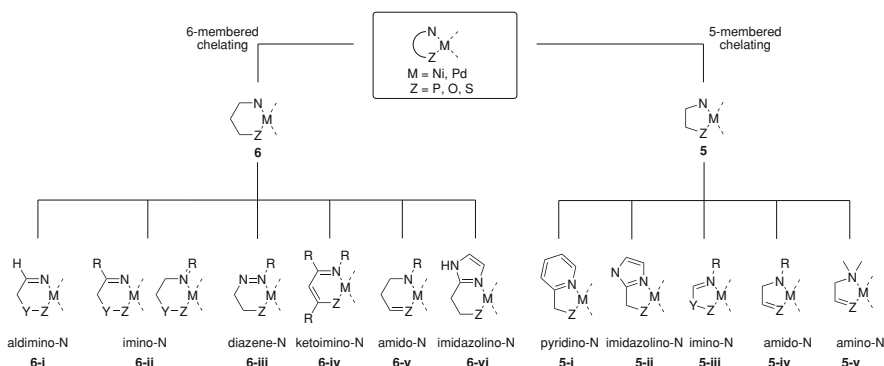


Fig. 2.1 Organization of Ni and Pd complexes with nitrogen-based mixed ligands according to the number of terms involved in metallacycle and the nature of nitrogen donor

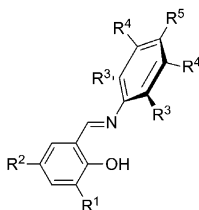
give polymers with relatively high molar masses. We anticipate that great part of this chapter will regard Ni and Pd transition-metal complexes with N–O ligands and their catalytic properties since those with N–P and especially with N–S mixed donor ligands have been relatively unexplored for olefin polymerization. This review organizes ligands in two main categories according to the number of terms involved in the forming metallacycles, 5- and 6-membered (Fig. 2.1), in general 4-membered rings are strained, whereas 7- or longer membered rings are not so much geometrically favoured.

2.2.1 N–O Ligands

Imino nitrogen is the most common donor function involved in 6-membered ring complexes especially for the high versatility as well as the simple synthesis that exploits conventional Schiff-base chemistry; both aldimino- (6-i) and imino-based (6-ii) complexes are of interest.

The most popular types are salicylaldimines (Fig. 2.2) on which N-aryl groups are installed via condensation reaction of proper aniline with aldehyde affording the corresponding bidentate ligand **A1–43**.

As carbonyl building blocks, the most studied are the salicylaldehydes [38–51], though also salicylketones appeared [52]. These scaffolds possess many sites of substitution allowing for the evaluation of both electronic and steric effects. Generally, electronic effects are investigated by introducing electron-withdrawing groups (NO_2 , CF_3), electron-donating groups (OMe , $t\text{Bu}$), or halogen atoms in both *o*- and *p*-position (R^{1-2}). In addition, the *o*-position (R^1) allows to take into account the steric effect of introducing bulky substituents such as anthracene or phenanthrene near to oxygen donor. In principle, basicity of imino-N can be directly tuned through imine backbone or indirectly by substitutes (R^{3-4-5}) on N-aryl moiety. These groups also play a crucial role by their steric hindrance.



- A1:** $R^1 = R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A2: $R^1 = \text{'Bu}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A3: $R^1 = \text{Ph}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A4: $R^1 = 9\text{-phen}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A5: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A6: $R^1 = R^4 = R^5 = H$; $R^2 = \text{MeO}$; $R^3 = \text{'Pr}$
A7: $R^1 = R^4 = R^5 = H$; $R^2 = \text{NO}_2$; $R^3 = \text{'Pr}$
A8: $R^1 = \text{trityl}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A9: $R^1 = m\text{-terp}$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$
A10: $R^1 = R^2 = I$; $R^3 = \text{'Pr}$; $R^4 = R^5 = H$
A11: $R^1 = \text{'Bu}$; $R^2 = \text{Me}$; $R^3 = \text{'Pr}$; $R^4 = R^5 = H$
A12: $R^1 = R^2 = \text{NO}_2$; $R^3 = \text{'Pr}$; $R^4 = R^5 = H$
A13: $R^1 = R^2 = \text{NO}_2$; $R^3 = R^4 = R^5 = H$
A14: $R^1 = R^2 = I$; $R^3 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$; $R^4 = R^5 = H$
A15: $R^1 = R^2 = I$; $R^3 = 3\text{-NO}_2\text{C}_6\text{H}_4$; $R^4 = R^5 = H$
A16: $R^1 = R^2 = I$; $R^3 = \text{C}_6\text{H}_5$; $R^4 = R^5 = H$
A17: $R^1 = R^2 = I$; $R^3 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$; $R^4 = R^5 = H$
A18: $R^1 = R^2 = I$; $R^3 = 3,5\text{-(MeO)}_2\text{C}_6\text{H}_3$; $R^4 = R^5 = H$
A19: $R^1 = \text{Cy}$; $R^2 = \text{Me}$; $R^3 = \text{'Pr}$; $R^4 = R^5 = H$
A20: $R^1 = \text{Cy}$; $R^2 = \text{Cl}$; $R^3 = \text{'Pr}$; $R^4 = R^5 = H$
A21: $R^1 = R^2 = I$; $R^3 = 4\text{-C}_6\text{F}_{17}\text{C}_6\text{H}_4$; $R^4 = R^5 = H$
A22: $R^1 = R^2 = I$; $R^3 = 4\text{-CF}_3\text{C}_6\text{H}_4$; $R^4 = R^5 = H$
A23: $R^1 = R^2 = R^3 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$; $R^4 = R^5 = H$
A24: $R^1 = R^2 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$; $R^3 = 4\text{-C}_6\text{F}_{17}\text{C}_6\text{H}_4$; $R^4 = R^5 = H$
A25: $R^1 = R^2 = I$; $R^3 = 3,5\text{-Bu}_2\text{C}_6\text{H}_3$; $R^4 = R^5 = H$
A26: $R^1 = R^2 = I$; $R^3 = 3,5\text{'Bu}_2\text{-4-OHC}_6\text{H}_2$; $R^4 = R^5 = H$
A27: $R^1 = R^2 = I$; $R^3 = 3,5\text{-Me}_2\text{-4-MeOC}_6\text{H}_2$; $R^4 = R^5 = H$
A28: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$
A29: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{'Bu}_2\text{C}_6\text{H}_3$
A30: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{'Bu}_2\text{-4-OHC}_6\text{H}_2$
A31: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$
A32: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{-Me}_2\text{-4-MeOC}_6\text{H}_2$
A33: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
A34: $R^1 = 9\text{-anth}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,4,5\text{-(MeO)}_3\text{C}_6\text{H}_2$
A35: $R^1 = R^4 = R^5 = H$; $R^2 = \text{NO}_2$; $R^3 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$
A36: $R^1 = \text{'Bu}$; $R^2 = R^4 = R^5 = H$; $R^3 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$
A37: $R^1 = R^2 = I$; $R^3 = 4\text{-FC}_6\text{H}_4$; $R^4 = R^5 = H$
A38: $R^1 = R^2 = I$; $R^3 = 4\text{-MeC}_6\text{H}_4$; $R^4 = R^5 = H$
A39: $R^1 = R^2 = I$; $R^3 = 4\text{-MeOC}_6\text{H}_4$; $R^4 = R^5 = H$
A40: $R^1 = R^2 = I$; $R^3 = 4\text{'BuC}_6\text{H}_4$; $R^4 = R^5 = H$
A41: $R^1 = R^2 = I$; $R^3 = 4\text{-Me}_2\text{NC}_6\text{H}_4$; $R^4 = R^5 = H$
A42: $R^1 = R^2 = R^3 = R^5 = R^6 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$; $R^4 = H$
A43: $R^1 = \text{NO}_2$; $R^2 = R^4 = R^5 = H$; $R^3 = \text{'Pr}$

Fig. 2.2 Salicylaldimine ligands reported in academic articles

Recently, another possible way to influence electronic properties of oxygen donor was introduced by replacing the anionic aryloxide moiety by a neutral pyridine N-oxide fragment affording ligands **B1-6** [53] (Fig. 2.3).

In addition, different approaches were proposed to incorporate two phenoxyimine chelating units affording binucleating ligands. Properly designed spacing units such as bisamines or bisaldehydes can be used for the purpose. Several bisamines were prepared and used as building blocks to prepare ditopic ligands [54–60]. A first class (**C1–12**) bears two amino moieties onto the same phenyl ring [54, 55]. Other spacers bearing two amino groups onto different phenyl rings were designed onto biphenyl (**C13–14**, **C17**), benzylphenyl (**C15–16**, **C18–20**), and terphenyl fragments (**C21–22**) [56]. In the bis-salicylaldimine ligand **C23** [59], which derives from the 3,3'-bisalicylaldimine scaffold, the two *o*-positions of oxygen donors are mutually hindered allowing for skipping synthetic steps to introduce bulky groups in such a crucial position. Ideally, naphthyloxy dialdehyde can be considered as constituted by two condensed salicylaldehydes. The corresponding N-aryl naphthyloxydiimine ligand **C24** possesses the unique feature of having two adjacent crabs [60] (Fig. 2.4).

Another strategy for generating imino groups in conjugation with an oxygen donor, specifically a carboxylic group, consists in reacting anthranilic acid with ketones yielding iminocarboxylato ligands **D1–3** [61] (Fig. 2.5).

Fig. 2.3 Selected 2-iminopyridine *N*-oxides ligands

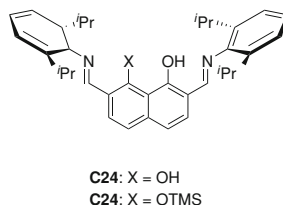
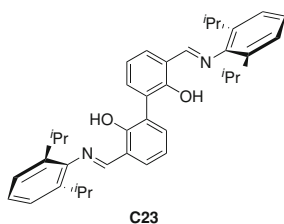
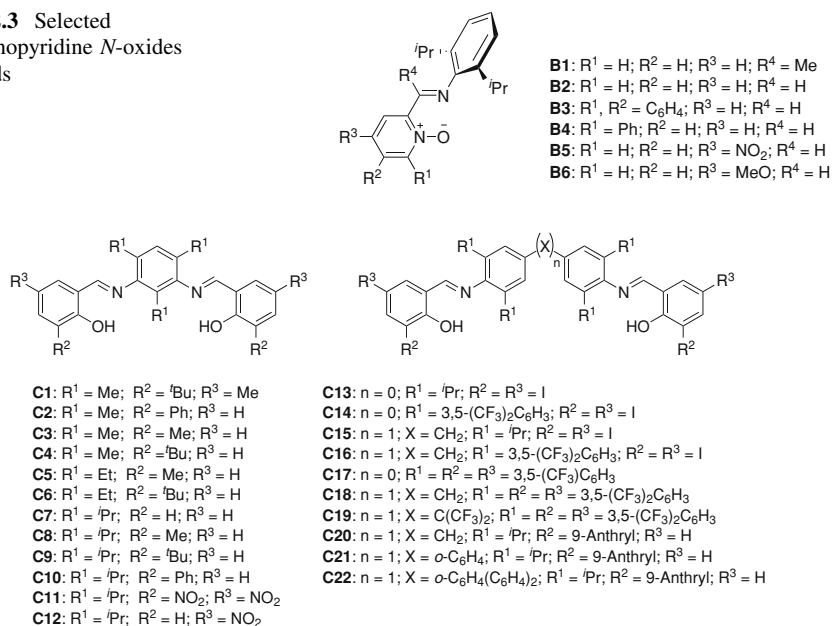
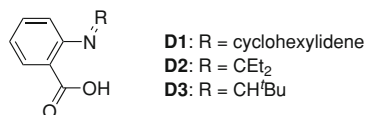


Fig. 2.4 Ditopic aldimine ligands

Fig. 2.5 Iminocarboxylic ligands



Alternatively, in ligands **E1–3** the imine fragment is replaced by a diazene (-N=N-) donor function. This family of ligands can be prepared via azo coupling of aniline with aromatic alcohols. Though little explored, these scaffolds offer, at least in principle, the same versatility and availability of substitution sites of salicylaldehydes [62] (Fig. 2.6).

Also enamines, which are the tautomeric form of imines, can be considered as practical building blocks in N–O ligand synthesis. Stabilization offered by conjugated ketones affords β -ketoimines **F1–17**, that is the conjugated acid of the monoanionic chelating β -ketoiminato ligand (6-iv). Similarly to salicylalimine,

these strong π ligands allow for selectively tuning electronic properties and steric demand. Electron-withdrawing substituents such as CF_3 , and $\text{CF}_3\text{C}=\text{O}$ are commonly added to the ketoimino backbone to reduce π -donation and enhance π -accepting abilities of the ligand, in order to increase the electrophilicity of the chelated metal. Steric bulk of the ligand can be amplified through both N-aryl moiety and R^1 fragment. According to the chemistry of enamines, methods of synthesis are somewhat more sophisticated than the usual Schiff condensation exploited in imine preparation and harsh conditions or activated synthones are required, especially when electron poor reagents are involved [63–68] (Fig. 2.7).

Other rare examples of 6-membered chelating ligands bear: (1) amino nitrogen in combination with an aldehyde oxygen donor (**G1**) [69]; (2) imidazole-based nitrogen donor in combination with a charged phenolato donor (**G2**) [70] (Fig. 2.8).

The length of the connecting bridge between two donor atoms in bidentate ligands plays a pivotal role in catalysis and it is tightly connected with the preferential coordination mode. The flexibility (elsewhere referred as plasticity) of a ligand can influence a catalytic reaction by stabilizing or destabilizing initial, transition, or final states and different coordination modes. In catalytic polymerization side reactions such as chain transfers, chain releasing, and displacements

Fig. 2.6 Diazene-naphthol ligands

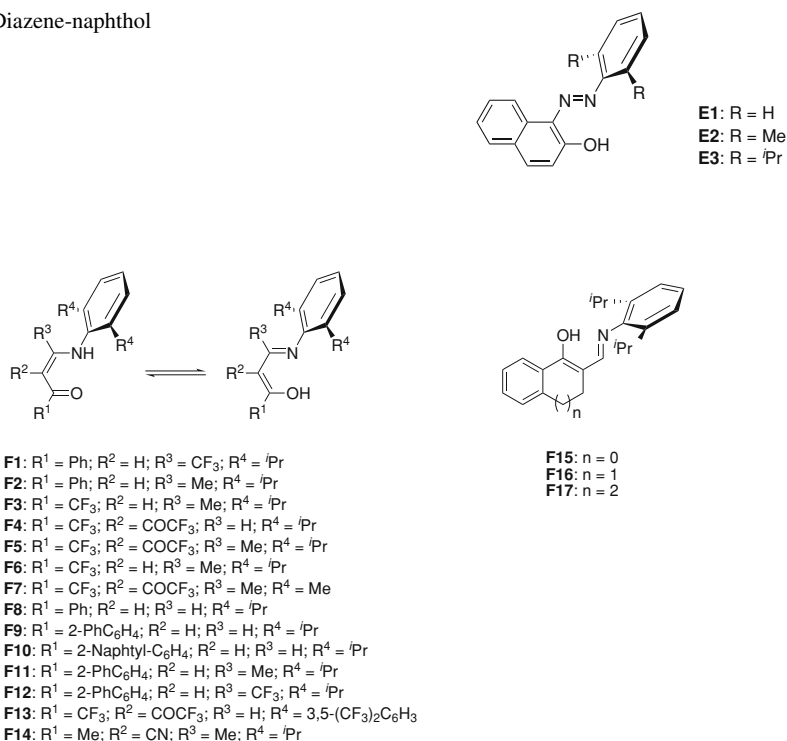


Fig. 2.7 Selected β -ketoimine ligands

can involve changes in catalyst geometry. Hence a limited flexibility in chelating ligand can in principle prevent side reactions and in turn increase TOF.

As a general rule, 5-membered chelated complexes are significantly more stable than the 6-membered homologs, especially for square-planar and octahedral complexes. The shorter spacer between the two donor atoms in pro-5-membered chelating ligands best meets the L-M-L angle of 90° preferred by square-planar (and octahedral) complexes. A higher thermodynamical stability prevents ligand displacement involved in catalyst deactivation pathways. Therefore, there is a strong interest in developing catalysts with N–O mixed ligands which possess a 5-membered chelate ring.

Indeed, early research on mixed N–O chelating ligands as components in polymerization catalysts refer to the very simple pyridine carboxylate ligands **H1–4** (5-i) [71, 72]. By introducing electron withdrawing or donating group onto aryl unit of ancillary chelating ligands electronic effects were considered. In any case, both the simple scaffold and the not modifiable carboxylato ligand did not allow an evaluation of steric effects. Other heterocycle-based ligands involve imidazole in combination with carboxylic (**H5–6**) and alcoholic (**H7**) donors [70] (Fig. 2.9).

While imine nitrogen donors dominate the field of 6-membered chelating ligands there are only few cases of the smaller 5-membered ring ligands involving imine as donor. A special case is represented by α -iminocarboxamide ligand **I1–9** [73–75] in which the imine donor is supported by an amide fragment. A number of these ligands was prepared by combining pyruvamides or other 2-oxo-substituted amides analogous with proper aniline. Binding mode of the ligand (N–N or N–O) depends upon the steric hindrance of aryl moieties and tends to N–O when it is sufficiently large (Fig. 2.10).

A rare neutral example of imino-based ligands is designed on the backbone of O-alkyl ester of iminohydroxamic acid. By iminoacylation of N,O-bisalkyl-hydroxylamines the corresponding bidentate ligands **L1–4** can be readily obtained [76] (Fig. 2.11).

Fig. 2.8 Aminoketone (**G1**) and 2-imidazolinophenol (**G2**) ligands

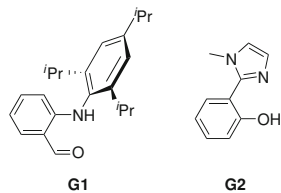


Fig. 2.9 5-membered chelating ligands containing N-heterocycles

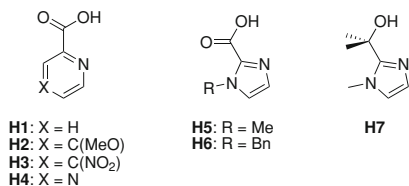
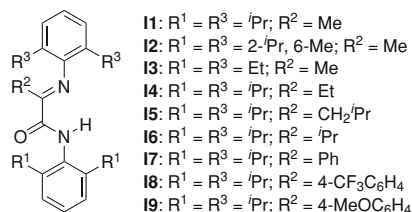
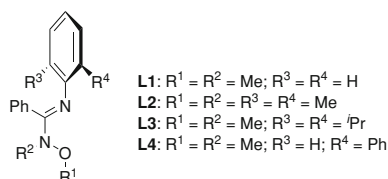


Fig. 2.10 α -imino-carboxamide ligands**Fig. 2.11** Bisalkyl-hydroxylamines ligands

More frequent are the ligands that bear vinylogous amido nitrogen donors (5-iii). This family includes 2-anilino-tropone-based ligands **M1–14** whose synthesis exploits the palladium catalyzed cross-coupling of aniline with 2-triflatotropone [77–79]. Several variations can be introduced by using hindered or electron poor N-aryl group and modified tropone skeleton. A similar synthetic approach was reported for the preparation of anilinoperinaphthenone-based ligands **N1–2** [80]. These ligands possess as additional feature the impossibility of delocalizing a negative charge onto oxygen donor upon deprotonation (Fig. 2.12).

Similar ligands can be prepared by using hydroxyquinones as carbonyl building blocks. Reaction with proper amine by vinylogous nucleophilic substitution readily affords the mono **O1–4** [81, 82] or binucleating **P1–5** ligands [83]. Also classical α -amino carboxylates can be in principle used as N–O-chelate ligands **Q1–4** (Fig. 2.13).

2.2.2 N–P and N–S Ligands

Imino groups can be tethered to a phosphine-based donor function affording bidentate iminophosphine ligands **R1–9**. They constitute important chiral P–N bidentate ligands for asymmetric catalysis by metal complexes [37] and appear in patents regarding olefin polymerization [85, 86]. These ligands are readily prepared by Schiff condensation of the corresponding amine and the aldehyde bearing the phosphine group. Besides sites of substitution on aromatic scaffold of the ligand also substituents at the phosphorus atom are accessible [87–89]. Alternatively the P donor can be combined with an amide fragment affording the diphenylphosphanylbenzamide ligand **S1–5** [90] (Fig. 2.14).

Pyridine-based 5-membered chelating ligands **T1–2** were prepared by Suzuki coupling of chloropicoline with mesitylboronic acid followed by diarylphospinylation at the α -position (Fig. 2.15).

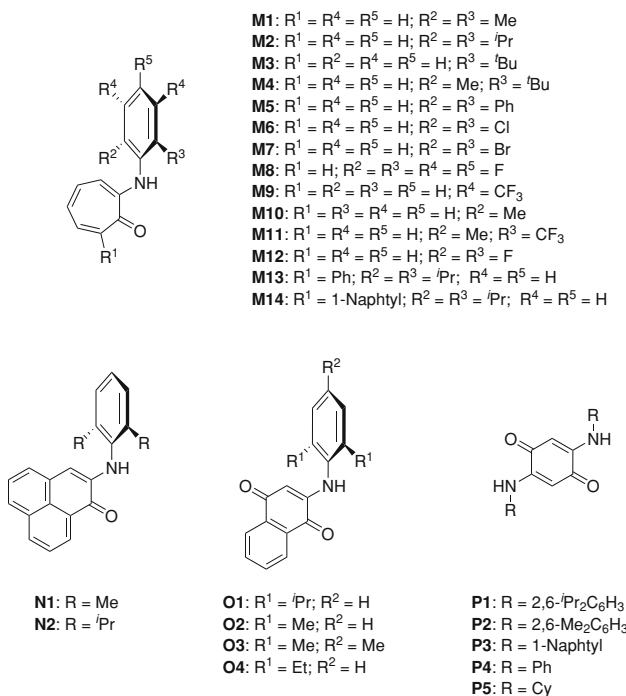


Fig. 2.12 Vinylogous amido-based ligands

Fig. 2.13 α -aminoacids investigated as ligands for catalysts for ethylene polymerization

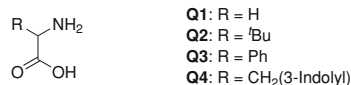


Fig. 2.14 Iminophosphine (**R1-9**) and diphenylphosphanylbenzamide (**S1-5**) ligands

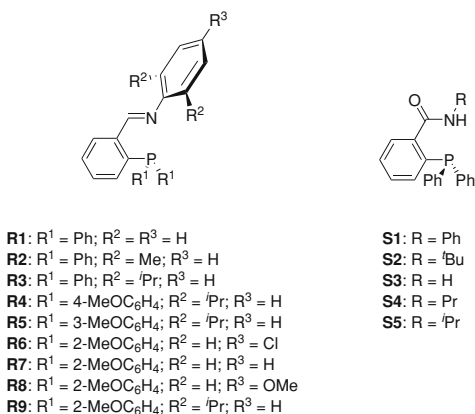
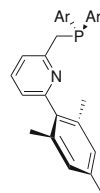
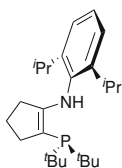
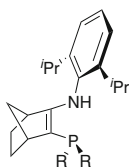
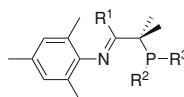


Fig. 2.15 Selected pyridinophosphine ligands

T1: Ar = 2,4,6-Me₃C₆H₂
T2: Ar = 2-MeC₆H₄

**U1**

U2: R = *t*Bu
U3: R = Ph



V1: R¹ = Ph; R² = R³ = Me
V2: R¹ = R² = R³ = Ph
V3: R¹ = H; R² = Me; R³ = 2,4,5-Me₃C₆H₂
V4: R¹ = Ph; R² = Me; R³ = 2,4,5-Me₃C₆H₂
V5: R¹ = Ph; R² = R³ = 2-MeC₆H₄

Fig. 2.16 R-phosphine enamines (**U1-3**) and phosphinoimine (**V1-5**) ligands

Imino nitrogen can be also tethered to a phosphine moiety through a bridging group in 5-membered chelating ligands. A family of ligands, which exists as R-phosphine enamines before complexation to Ni(II) or Pd(II) and affords phosphine imine by tautomerization, was successfully prepared by nucleophilic substitution of bisalkylchlorophosphine by imine anions [91]. Monocyclic (**U1**) and bicyclic (**U2-3**) backbones were used to enhance the conformational rigidity and prevent ligand displacement [34]. Both bulky *ortho* substituents on the aniline moieties and bulky phosphines were introduced to supply the steric requirement that is crucial for obtaining high molar mass polymers.

Nonenolizable bulky phosphine imine bidentate ligands **V1-5** [35] can be prepared by installing a *gem*-dimethyl group α to phosphorus. Ligands can be obtained by direct nucleophilic attack of the azaenolate to the phosphorus electrophiles R₂PCl (R = Me, Ph). In the case of higher hindered mesityl-substituted-P compounds the azaenolate was reacted with MesPCl₂ followed by the Grignard reagent MeMgBr to introduce other substituents on phosphorous. Otherwise, reaction occurred at both carbon and nitrogen of the azaenolate, yielding a mixture of isomers. The purity and yield of the ligands can be estimated from the ³¹P NMR spectra (Fig. 2.16).

Ideally, the most straightforward modification of diimine ligands consists in replacing one imine moiety with a phosphinidine. Nucleophilic attack of deprotonated imine to mesityl-PCl₂ followed by elimination of HCl affords ligands **W1-2** (Fig. 2.17) [92].

Fig. 2.17 Phosphinidine-imine-based ligands

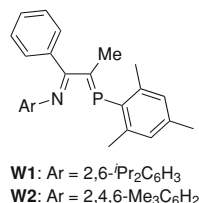
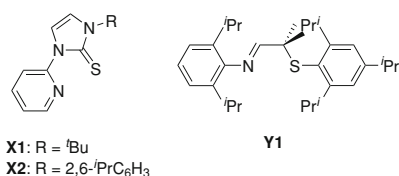


Fig. 2.18 Imidazole-2-thione (**X1-2**) and imine-sulfide (**Y1**) ligands



Despite the intensive research on catalysts with hard-and-soft mixed ligands for olefin oligomerization or polymerization, examples of N–S ligands remain scarce (Fig. 2.18). A family of 6-membered chelating ligands combines pyridine donor with imidazole-2-thione moieties affording the corresponding bidentate N–S ligands **X1–2** [93].

The single case of a 5-membered chelating ligand refers to the imine-sulfide ligand **Y1**, which is prepared from the condensation of the corresponding α -thioaldehyde with 2,6-diisopropylaniline [92].

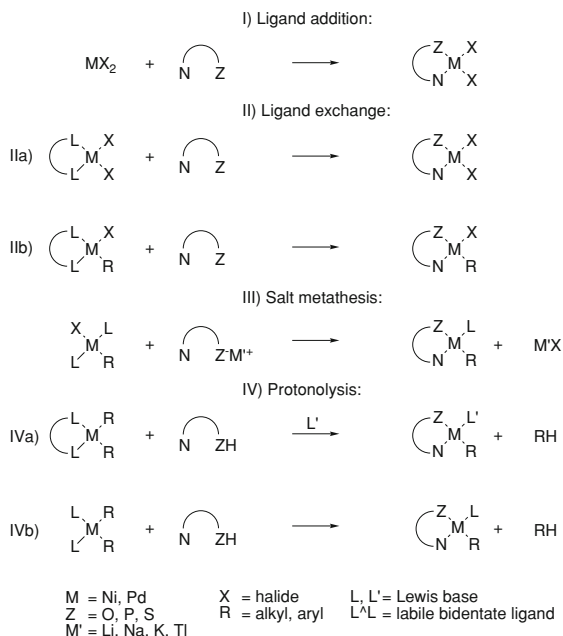
2.3 Group X Metal Complexes

Ni and Pd compounds with mixed ligands (N–Z) exploited as catalysts for olefin (co)polymerization are generally 16 electron square planar complexes. Asymmetry of the chelating mixed ligand as well as diversity of the ligands completing the coordination sphere of the metal cause distortion of complexes from ideal square planar geometry (D_{4h}). Definitely, one of the key features of these complexes is *trans*-effect, and in turn *trans*-influence. The former drives their synthesis and final structure, the latter deeply influences their reactivity. Different synthetic approaches are used to prepare Ni and Pd complexes with mixed ligands depending on the nature of the ligand as well as the features of the final complex (Fig. 2.19).

Even dihalide complexes are seldom achieved by direct ligand addition to dihalide metal salt (I). They are in general synthesized by ligand displacement reaction between the chelating ligand and a proper metal precursor, containing an isoelectronic labile bidentate ligand such as dme or tmeda (IIa). The major driving force is the higher stability furnished by π -accepting frameworks in chelating ligand with respect to the pure σ -donors in the ligand precursors.

Hydrocarbyl complexes are generally prepared by using alkyl-containing metal sources rather than converting the dihalo-compounds into the corresponding metal

Fig. 2.19 General synthetic routes to Ni and Pd complexes with N–Z ligands



alkyls by nucleophilic attack. This avoids the partial reduction of metal with consequent loss of mixed chelating ligand or undesired reactions of mixed ligand with the alkylating agent.

The selection of the metal precursor depends on the charge of mixed chelating ligand, which influences the method of synthesis employed. Thus, neutral mixed ligands can be installed by ligand exchange on metal precursors (IIb) built with an alkyl fragment (R), an anionic donor such as halide (X), and a leaving neutral chelating ligand (L–L). In the resulting hydrocarbyl complexes the alkyl fragment will possess a *cis*-anionic donor.

Most commonly, the installing mixed ligands are anionic (N–Z[−]) and synthesis occurs via salt metathesis (III) or protonolysis (IV).

Salt metathesis (III) between precursor and the salt of anionic ligand, which is commonly obtained by deprotonation with alkali hydride, is the most used synthesis for complexes containing mixed ligands, one alkyl group, and a Lewis base. In this case the precursor should be able to lose one anionic ligand (X[−]), which is eliminated as salt, commonly an alkaline halide salt, and a neutral ligand that is replaced by the mixed chelating ligand. Trans labilizing effect of the alkyl group drives the synthesis and the resulting complex contains the nitrogen ligand trans to the Lewis base, with few exceptions, due to high steric hindrance.

Alternatively, the protonolysis approach uses acid ligands and bis-hydrocarbyl precursors affording the desired organometallic complexes by sacrificing one hydrocarbyl ligand. This strategy is frequently accomplished by a concomitant ligand exchange to substitute a bidentate Lewis base with a monodentate ligand

(IVa). Otherwise, Lewis bases can be already present in the precursor and displaced by the neutral fragment of the mixed ligand (IVb). Again, trans effect affords complexes with nitrogen ligands trans to the Lewis bases.

The reported methods for the synthesis of Ni and Pd complexes are summarized in Fig. 2.19 and they will be referred with the corresponding keys in Table 2.1.

2.4 Application in Homogeneous Catalyzed Polymerization

2.4.1 Activation

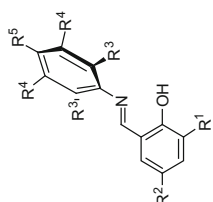
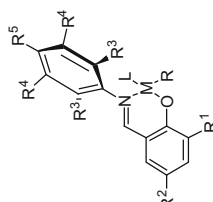
The Ni and Pd complexes with mixed N–O, N–S, and N–P chelating ligands listed in Table 2.1 are catalyst precursors which need to be activated to yield the species active for the polymerization. Such N–Z ligands must be coordinated to the metal also in the active species to effectively control catalyst selectivity and activity via steric and electronic interactions.

In general, it is the cationic form of organometallic complexes that is of interest in polymerizations, generated from catalyst precursors by activation with a cocatalyst. The most frequently used cocatalysts are aluminoxanes such as MAO or derivatives (MMAO) [94, 95]. The role of MAO includes alkylation of dihalides, subsequent abstraction of a ligand to form the cationic complex, and the scavenging of impurities. Other important cocatalysts for precursors containing alkyl or aryl ligands are perfluorinated boranes, such as $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. Often aluminum alkyls (AlR_3 with $\text{R} = ^i\text{Bu}$, $n\text{-C}_6\text{H}_{13}$) are employed together with the cocatalyst.

All Ni and Pd dihalide catalyst precursors with neutral N–Z ligands and in some case even the more sophisticated precursors bearing anionic N–Z ligands, which are already alkylated, can be activated by aluminum-based cocatalysts (Fig. 2.20). Discrete cationic alkyl complexes of palladium and nickel are synthesized by reaction with a variety of salts of noncoordinating anions to yield cationic organometallic species.

In the general structure the ‘stabilizing’ ligands L allows for facile removal from the metal center, e.g. by displacement by coordination of olefin monomer; L is most often neutral, while the ligand R bound to the metal via a carbon atom enables facile entry into the catalytic cycle. When the cationic species is generated in situ in the presence of the olefin, the L' may also be a solvent molecule or the olefin monomer. Y^- is very weakly or non-coordinating to avoid interactions with the metal center, leading e.g. to displacement of labile ligands L' or to strong coordination blocking the sites during catalysis. As alkyl complexes of late transition metals easily give β -hydride elimination, often R alkyl substituents do not have β -H atoms, or for steric reasons do not allow β -H eliminations. Anyhow, among the listed precursors halo and alkyl complexes activated as metallocenes and diimine catalysts are rare.

Table 2.1 Synthetic routes to Ni and Pd complexes with N-O, N-P, and N-S ligands

Metal precursor	Ligand	Method	Catalyst	No. References	
6-membered chelated complexes with N-O ligands					
[Ni(Cl)(Ph)(PPh ₃) ₂]		III		A1 R ¹ = R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr	1 [38]
	A2 R ¹ = <i>i</i> Bu; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr			2	
	A3 R ¹ = Ph; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr			3	
	A4 R ¹ = 9-phen; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr			4	
	A5 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr			5	
	A6 R ¹ = R ⁴ = R ⁵ = H; R ² = MeO; R ³ = <i>i</i> Pr			6	
	A7 R ¹ = R ⁴ = R ⁵ = H; R ² = NO ₂ ; R ³ = <i>i</i> Pr			7	
[Ni(tmeda)Me ₂]	A5 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr	IVa	[Ni(A5)Me(MeCN)]	8 [39]	
	A8 R ¹ = trityl; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr		[Ni(A8)Me(MeCN)]	9	
	A9 R ¹ = <i>m</i> -terp; R ² = R ⁴ = R ⁵ = H; R ³ = <i>i</i> Pr		[Ni(A9)Me(MeCN)]	10	
[Ni(Cl)(Ph)(PPh ₃) ₂] [Ni(tmeda)Me ₂]	A10 R ¹ = R ² = I; R ³ = <i>i</i> Pr; R ⁴ = R ⁵ = H	II	[Ni(A10)Ph(PPh ₃)]	11 [40]	
	A10	IVa	[Ni(A10)Me(py)]	12	

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
$[\text{Ni}(\eta^3\text{-C}_3\text{H}_5\text{Br})_2]$	A11 $\text{R}^1 = \text{'Bu}; \text{R}^2 = \text{Me}; \text{R}^3 = \text{'Pr}; \text{R}^4 = \text{R}^5 = \text{H}$	a	$[\text{Ni}_2(\text{A11})_2(\mu\text{-OH})_2]$	13 [41]
$\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$	A11	I	$[\text{Ni}_2(\text{A11})_2(\mu\text{-OH})_2]$	13
$[\text{Ni}(\text{acac})_2]$	A11	IIa	$[\text{Ni}(\text{A11})(\text{acac})]$	14
$[\text{Ni}(\text{dme})\text{Br}_2]$	A11	b	$[\text{Ni}(\text{A11})_2]$	15
$[\text{Ni}(\text{dme})\text{Cl}_2]$	A11	c	$[\text{Ni}(\text{A11})\text{Me}]^+$ (in situ)	16
$[\text{Ni}(\text{cod})_2]$	A3 $\text{R}^1 = \text{Ph}; \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}; \text{R}^3 = \text{'Pr}$ A7 $\text{R}^1 = \text{R}^4 = \text{R}^5 = \text{H}; \text{R}^2 = \text{NO}_2; \text{R}^3 = \text{'Pr}$ A12 $\text{R}^1 = \text{R}^2 = \text{NO}_2; \text{R}^3 = \text{'Pr}; \text{R}^4 = \text{R}^5 = \text{H}$ A13 $\text{R}^1 = \text{R}^2 = \text{NO}_2; \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$ A14 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3; \text{R}^4 = \text{R}^5 = \text{H}$	d	$[\text{Ni}(\text{A3})(\text{cod})]$ $[\text{Ni}(\text{A7})(\text{cod})]$ $[\text{Ni}(\text{A12})(\text{cod})]$ $[\text{Ni}(\text{A13})(\text{cod})]$	17 [42] 18 19 20
$[\text{Ni}(\text{tmeda})\text{Me}_2]$	A15 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = 3\text{-NO}_2\text{C}_6\text{H}_4; \text{R}^4 = \text{R}^5 = \text{H}$ A16 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = \text{Ph}; \text{R}^4 = \text{R}^5 = \text{H}$ A17 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = 3,5\text{-Me}_2\text{C}_6\text{H}_3; \text{R}^4 = \text{R}^5 = \text{H}$ A18 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = 3,5\text{-(MeO)}_2\text{C}_6\text{H}_3; \text{R}^4 = \text{R}^5 = \text{H}$	IVa	$[\text{Ni}(\text{A14})\text{Me}(\text{py})]$ $[\text{Ni}(\text{A15})\text{Me}(\text{py})]$ $[\text{Ni}(\text{A16})\text{Me}(\text{py})]$ $[\text{Ni}(\text{A17})\text{Me}(\text{py})]$	21 [44] 22 23 24
$[\text{NiCl}(\text{Ph})(\text{PPh}_3)_2]$	A19 $\text{R}^1 = \text{Cy}; \text{R}^2 = \text{Me}; \text{R}^3 = \text{'Pr}; \text{R}^4 = \text{R}^5 = \text{H}$	III	$[\text{Ni}(\text{A18})\text{Me}(\text{py})]$ $[\text{Ni}(\text{A19})\text{Ph}(\text{PPh}_3)]$	25 26 [45]
$[\text{NiCl}(\text{Ph})(\text{PPh}_3)_2]$	A20 $\text{R}^1 = \text{Cy}; \text{R}^2 = \text{Cl}; \text{R}^3 = \text{'Pr}; \text{R}^4 = \text{R}^5 = \text{H}$	III	$[\text{Ni}(\text{A20})\text{Ph}(\text{PPh}_3)]$	27 [46]
$[\text{Ni}(\text{tmeda})\text{Me}_2]$	A21 $\text{R}^1 = \text{R}^2 = \text{I}; \text{R}^3 = 4\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4; \text{R}^4 = \text{R}^5 = \text{H}$	IVa	$[\text{Ni}(\text{A21})\text{Me}(\text{py})]$	28 [47]

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(tmeda)Me ₂]	A22 R ¹ = R ² = I; R ³ = 4-CF ₃ C ₆ H ₄ ; R ⁴ = R ⁵ = H		[Ni(A22)Me(py)]	29
	A23 R ¹ = R ² = R ³ = 3,5-Me ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H		[Ni(A23)Me(py)]	30
	A24 R ¹ = R ² = 3,5-Me ₂ C ₆ H ₃ ; R ³ = 4-C ₈ F ₁₇ C ₆ H ₄ ; R ⁴ = R ⁵ = H		[Ni(A24)Me(py)]	31
	A5 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = ⁱ Pr	IVa	[Ni(A5)Me(py)]	32 [48]
	A25 R ¹ = R ² = I; R ³ = 3,5- ⁱ Bu ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H		[Ni(A25)Me(py)]	33
	A26 R ¹ = R ² = I; R ³ = 3,5- ⁱ Bu ₂ -4-OHC ₆ H ₂ ; R ⁴ = R ⁵ = H		[Ni(A26)Me(py)]	34
	A27 R ¹ = R ² = I; R ³ = 3,5-Me ₂ -4-MeOC ₆ H ₂ ; R ⁴ = R ⁵ = H		[Ni(A27)Me(py)]	35
	A28 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-(CF ₃) ₂ C ₆ H ₃		[Ni(A28)Me(py)]	36
	A29 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5- ⁱ Bu ₂ C ₆ H ₃		[Ni(A29)Me(py)]	37
	A30 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5- ⁱ Bu ₂ -4-OHC ₆ H ₂		[Ni(A30)Me(py)]	38
	A31 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-Me ₂ C ₆ H ₃		[Ni(A31)Me(py)]	39
	A32 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-Me ₂ -4-MeOC ₆ H ₂		[Ni(A32)Me(py)]	40

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(py) ₂ Me ₂]	A33 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-(MeO) ₂ C ₆ H ₃		[Ni(A33)Me(py)]	41
	A34 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,4,5-(MeO) ₃ C ₆ H ₂		[Ni(A34)Me(py)]	42
	A35 R ¹ = R ⁴ = R ⁵ = H; R ² = NO ₂ ; R ³ = 3,5-(CF ₃) ₂ C ₆ H ₃		[Ni(A35)Me(py)]	43
	A36 R ¹ = ^t Bu; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5- (CF ₃) ₂ C ₆ H ₃		[Ni(A36)Me(py)]	44
	A25 R ¹ = R ² = I; R ³ = 3,5- ⁱ Bu ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H	IVb	[Ni(A25)Me(py)]	33
	A26 R ¹ = R ² = I; R ³ = 3,5- ⁱ Bu ₂ -4-OHC ₆ H ₂ ; R ⁴ = R ⁵ = H		[Ni(A26)Me(py)]	34
	A27 R ¹ = R ² = I; R ³ = 3,5-Me ₂ -4-MeOC ₆ H ₂ ; R ⁴ = R ⁵ = H		[Ni(A27)Me(py)]	35
	A28 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-(CF ₃) ₂ C ₆ H ₃		[Ni(A28)Me(py)]	36
	A29 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5- ⁱ Bu ₂ C ₆ H ₃		[Ni(A29)Me(py)]	37
	A30 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5- ⁱ Bu ₂ -4-OHC ₆ H ₂		[Ni(A30)Me(py)]	38
	A32 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-Me ₂ -4-MeOC ₆ H ₂		[Ni(A32)Me(py)]	40

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(tmeda)Me ₂]	A33 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,5-(MeO) ₂ C ₆ H ₃		[Ni(A33)Me(py)]	41
	A34 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = 3,4,5-(MeO) ₃ C ₆ H ₂		[Ni(A34)Me(py)]	42
	A37 R ¹ = R ² = I; R ³ = 4-FC ₆ H ₄ ; R ⁴ = R ⁵ = H	IVa	[Ni(A37)Me(py)]	45 [49]
	A38 R ¹ = R ² = I; R ³ = 4-MeC ₆ H ₄ ; R ⁴ = R ⁵ = H	IVa	[Ni(A38)Me(py)]	46
	A39 R ¹ = R ² = I; R ³ = 4-MeOC ₆ H ₄ ; R ⁴ = R ⁵ = H		[Ni(A39)Me(py)]	47
	A40 R ¹ = R ² = I; R ³ = 4'-BuC ₆ H ₄ ; R ⁴ = R ⁵ = H		[Ni(A40)Me(py)]	48
	A41 R ¹ = R ² = I; R ³ = 4-Me ₂ NC ₆ H ₄ ; R ⁴ = R ⁵ = H		[Ni(A41)Me(py)]	49
	A42 R ¹ = R ² = R ³ = R ⁵ = 3,5-(CF ₃) ₂ C ₆ H ₃ ; R ⁴ = H	IVa	[Ni(A42)Me(py)]	50 [50]
	A5 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = ⁱ Pr	IVb	[Ni(A5)Me(tmeda)]	51
	A14 R ¹ = R ² = I; R ³ = 3,5-(CF ₃) ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H		[Ni(A14)Me(tmeda)]	52
	A23 R ¹ = R ² = R ³ = 3,5-Me ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H		[Ni(A23)Me(tmeda)]	53
	A42 R ¹ = R ² = R ³ = 3,5-Me ₂ C ₆ H ₃ ; R ⁴ = R ⁵ = H		[Ni(A42)Me(tmeda)]	54
	A43 R ¹ = NO ₂ ; R ² = R ⁴ = R ⁵ = H; R ³ = ⁱ Pr	III	[Ni(A43)Ph(PPh ₃)]	55 [51]
	A5 R ¹ = 9-anth; R ² = R ⁴ = R ⁵ = H; R ³ = ⁱ Pr	III	[Ni(A5)(η^1 -CH ₂ Ph)(PMe ₃) ₂]	56 [58]
[NiCl(Me)(PMe ₃) ₂]	A2 R ¹ = ⁱ Bu; R ² = R ⁴ = R ⁵ = H; R ³ = ⁱ Pr	III	[Ni(A2)(Me)(PMe ₃)]	57 [60]

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiCl(1-naph)(PPh ₃) ₂]	A2	III	[Ni(A2)(1-naph)(PPh ₃)]	58
[Ni(tmeda)Me ₂]	A14	IVa	[Ni(A14)Me(tppts)]	59 [103]
	A14		[Ni(A14)Me(tppts)]	60
	A14		[Ni(A14)Me(H ₂ N-PEG-OMe)]	61
	A26		[Ni(A26)Me(tppts)]	61
	A26		[Ni(A26)Me(tppts)]	62
	A28		[Ni(A28)Me(tppts)]	63
	A28		[Ni(A28)Me(H ₂ N-PEG-OMe)]	64
	A30		[Ni(A30)Me(tppts)]	65
	A30		[Ni(A30)Me(H ₂ N-PEG-OMe)]	66
[Ni(tmeda)Me ₂]	A14	IVa	[Ni(A14)Me(pta)]	67 [104]
	A14		[Ni(A14)Me(hmta)]	68
	A14		[Ni(A14)Me(3-Et ₄ NO ₃ -C ₅ H ₄ N)]	69
[Ni(tmeda)Me ₂]	A14	IVa	[Ni(A14)Me(dmso)]	70 [107]
[Ni(A14)Cl(PMe ₃)]	A14	e	[Ni(A14)H(PMe ₃)]	71

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(A14)Me(dmsol)]	A14	f	[Ni(A14)Et(dmsol)]	72
[Ni(dme)Br ₂]	B1 R ¹ = R ² = R ³ = H; R ⁴ = Me	IIa	[Ni(B1)Br ₂]	73 [53]
	B2 R ¹ = R ² = R ³ = R ⁴ = H			74
	B3 R ¹ , R ² = C ₆ H ₄ ; R ³ = R ⁴ = H			75
	B4 R ¹ = Ph; R ² = R ³ = R ⁴ = H			76
	B5 R ¹ = R ² = R ⁴ = H; R ³ = NO ₂			77
	B6 R ¹ = R ² = R ⁴ = H; R ³ = MeO			78
PdBr ₂	B4 R ¹ = Ph; R ² = R ³ = R ⁴ = H	I	[Pd(B4)Br ₂]	79 [53]
		III	[Ni ₂ (C1)(Ph) ₂ (PPh ₃) ₂]	80 [54]
[NiCl(Ph)(PPh ₃) ₂]	C1 R ¹ = Me; R ² = ^t Bu; R ³ = Me			

(continued)

Table 2.1 (continued)

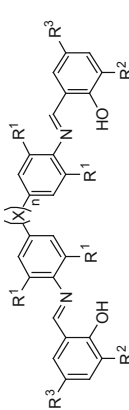
Metal precursor	Ligand	Method	Catalyst	No. References
[NiCl(Ph)(PPh ₃) ₂]	C2 R ¹ = Me; R ² = Ph; R ³ = H	III	[Ni ₂ (C2)(Ph) ₂ (PPh ₃) ₂]	81
	C3 R ¹ = Me; R ² = Me; R ³ = H		[Ni ₂ (C3)(Ph) ₂ (PPh ₃) ₂]	82 [55]
	C4 R ¹ = Me; R ² = ⁱ Bu; R ³ = H		[Ni ₂ (C4)(Ph) ₂ (PPh ₃) ₂]	83
	C5 R ¹ = Et; R ² = Me; R ³ = H		[Ni ₂ (C5)(Ph) ₂ (PPh ₃) ₂]	84
	C6 R ¹ = Et; R ² = ⁱ Bu; R ³ = H		[Ni ₂ (C6)(Ph) ₂ (PPh ₃) ₂]	85
	C7 R ¹ = ⁱ Pr; R ² = R ³ = H		[Ni ₂ (C7)(Ph) ₂ (PPh ₃) ₂]	86
	C8 R ¹ = ⁱ Pr; R ² = Me; R ³ = H		[Ni ₂ (C8)(Ph) ₂ (PPh ₃) ₂]	87
	C9 R ¹ = ⁱ Pr; R ² = ⁱ Bu; R ³ = H		[Ni ₂ (C9)(Ph) ₂ (PPh ₃) ₂]	88
	C10 R ¹ = ⁱ Pr; R ² = Ph; R ³ = H		[Ni ₂ (C10)(Ph) ₂ (PPh ₃) ₂]	89
	C11 R ¹ = ⁱ Pr; R ² = R ³ = NO ₂		[Ni ₂ (C11)(Ph) ₂ (PPh ₃) ₂]	90
	C12 R ¹ = ⁱ Pr; R ² = H; R ³ = NO ₂		[Ni ₂ (C12)(Ph) ₂ (PPh ₃) ₂]	91
[Ni(py) ₂ Me ₂]		IVb	[Ni ₂ (C13)Me ₂ (py) ₂]	92 [56]
	C14 n = 0; R ¹ = ⁱ Pr; R ² = R ³ = I		[Ni ₂ (C14)Me ₂ (py) ₂]	93
	C15 n = 1; X = CH ₂ ; R ¹ = ⁱ Pr; R ² = R ³ = I		[Ni ₂ (C15)Me ₂ (py) ₂]	94
	C16 n = 1; X = CH ₂ ; R ¹ = 3,5-(CF ₃) ₂ C ₆ H ₃ ; R ² = R ³ = I		[Ni ₂ (C16)Me ₂ (py) ₂]	95
				(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(tmeda)Me ₂]	C14 n = 0; R ¹ = 3,5-(CF ₃) ₂ C ₆ H ₃ ; R ² = R ³ = H	IVb	[Ni ₂ (C14)Me ₂ (tmeda) ₂]	96 [56]
[Ni(py) ₂ Me ₂]	C17 n = 0; R ¹ = R ² = R ³ = 3,5-(CF ₃)C ₆ H ₃	IVb	[Ni ₂ (C17)Me ₂ (py) ₂]	97 [57]
	C18 n = 1; X = CH ₂ ; R ¹ = R ² = R ³ = 3,5-(CF ₃)C ₆ H ₃		[Ni ₂ (C18)Me ₂ (py) ₂]	98
	C19 n = 1; X = C(CF ₃) ₂ ; R ¹ = R ² = R ³ = 3,5-(CF ₃) ₂ C ₆ H ₃		[Ni ₂ (C19)Me ₂ (py) ₂]	99
[Ni(η ³ -CH ₂ Ph)Cl(PMe ₃)]	C20 n = 1; X = CH ₂ ; R ¹ = ⁱ Pr; R ² = 9-Anth; R ³ = H	III	[Ni ₂ (C20)(η ¹ -CH ₂ Ph)(PMe ₃) ₂]	100 [58]
	C21 n = 1; X = o-C ₆ H ₄ ; R ¹ = ⁱ Pr; R ² = 9-Anth; R ³ = H		[Ni ₂ (C21)(η ¹ -CH ₂ Ph)(PMe ₃) ₂]	101
	C22 n = 1; X = o-C ₆ H ₄ (C ₆ H ₄) ₂ ; R ¹ = ⁱ Pr; R ² = 9-Anth; R ³ = H		[Ni ₂ (C22)(η ¹ -CH ₂ Ph)(PMe ₃) ₂]	102
	C23 Ar = 2,6- ⁱ PrC ₆ H ₃	III	[Ni ₂ (C23)(Ph) ₂ (PPh ₃) ₂]	103 [59]

(continued)

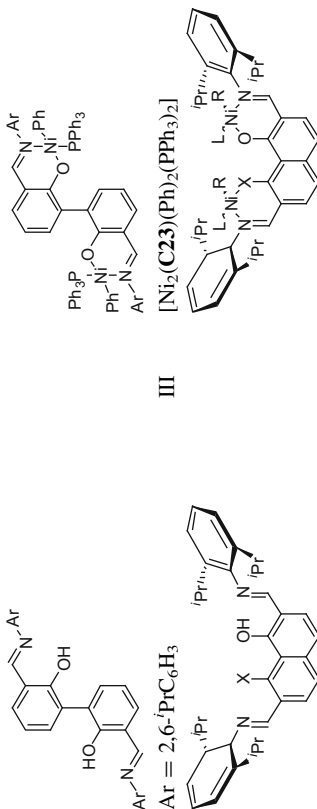
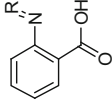
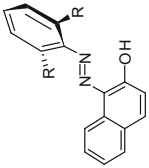
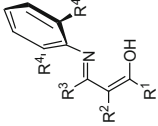


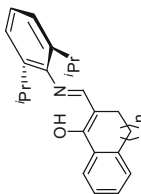
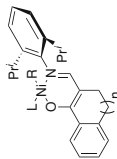
Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiClMe(PMe ₃) ₂]	C24 X = OH	III	[Ni ₂ (C24)Me ₂ (PMe ₃) ₂]	104 [60]
[NiClMe(PPh ₃) ₂]	C24 X = OH		[Ni ₂ (C24)Me ₂ (PPh ₃) ₂]	105
[NiCl(1-naph)(PPh ₃) ₂]	C24 X = OH		[Ni ₂ (C24)(1-naph) ₂ (PPh ₃) ₂]	106
	C25 X = OTMS		[Ni(C25)(1-naph)(PPh ₃)]	107
				
[Ni(η ³ -CH ₂ CMech ₂)Cl] ₂	D1 R = cyclohexylidene	III	[Ni(D1)(η ³ -CH ₂ CMech ₂)]	108 [61]
[Ni(η ³ -CH ₂ Ph)Cl(PMe ₃)]	D1		[Ni(D1)(η ³ -CH ₂ Ph)]	109
	D2 R = CEt ₂		[Ni(D2)(η ³ -CH ₂ Ph)]	110
				
[Ni(tmeda)Me ₂]	E1 R = H	IVa	[Ni(E1)Me(py)]	111 [62]
	E2 R = Me		[Ni(E2)Me(py)]	112
	E3 R = ⁱ Pr		[Ni(E3)Me(py)]	113
				
[NiCl(Ph)(PPh ₃) ₂]	F1 R ¹ = Ph; R ² = H; R ³ = CF ₃ ; R ⁴ = ⁱ Pr	III	[Ni(F1)(Ph)(PPh ₃)]	114 [63]
	F2 R ¹ = Ph; R ² = H; R ³ = Me; R ⁴ = ⁱ Pr		[Ni(F2)(Ph)(PPh ₃)]	115

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiCl(Ph)(PPh ₃) ₂]	F3 R ¹ = CF ₃ ; R ² = H; R ³ = Me; R ⁴ = <i>i</i> Pr	III	[Ni(F3)(Ph)(PPh ₃)]	116
	F4 R ¹ = CF ₃ ; R ² = COCF ₃ ; R ³ = H; R ⁴ = <i>i</i> Pr		[Ni(F4)(Ph)(PPh ₃)]	117 [64]
	F5 R ¹ = CF ₃ ; R ² = COCF ₃ ; R ³ = Me; R ⁴ = <i>i</i> Pr		[Ni(F5)(Ph)(PPh ₃)]	118
	F6 R ¹ = CF ₃ ; R ² = H; R ³ = Me; R ⁴ = <i>i</i> Pr		[Ni(F6)(Ph)(PPh ₃)]	119
	F7 R ¹ = CF ₃ ; R ² = COCF ₃ ; R ³ = Me; R ⁴ = Me		[Ni(F7)(Ph)(PPh ₃)]	120
[NiCl(Ph)(PPh ₃) ₂]	F8 R ¹ = Ph; R ² = H; R ³ = H; R ⁴ = <i>i</i> Pr	III	[Ni(F8)(Ph)(PPh ₃)]	121 [65]
	F9 R ¹ = 2-PhC ₆ H ₄ ; R ² = H; R ³ = H; R ⁴ = <i>i</i> Pr		[Ni(F9)(Ph)(PPh ₃)]	122
	F10 R ¹ = 2-Naph-C ₆ H ₄ ; R ² = H; R ³ = H; R ⁴ = <i>i</i> Pr		[Ni(F10)(Ph)(PPh ₃)]	123
	F11 R ¹ = 2-PhC ₆ H ₄ ; R ² = H; R ³ = Me; R ⁴ = <i>i</i> Pr		[Ni(F11)(Ph)(PPh ₃)]	124
	F12 R ¹ = 2-PhC ₆ H ₄ ; R ² = H; R ³ = CF ₃ ; R ⁴ = <i>i</i> Pr		[Ni(F12)(Ph)(PPh ₃)]	125
[Ni(tmeda)Me ₂]	F4 R ¹ = CF ₃ ; R ² = COCF ₃ ; R ³ = H; R ⁴ = <i>i</i> Pr	IVa	[Ni(F4)Me(py)]	126 [66]
	F13 R ¹ = CF ₃ ; R ² = COCF ₃ ; R ³ = H; R ⁴ = 3,5-(CF ₃) ₂ C ₆ H ₃		[Ni(F13)Me(py)]	127
[Ni(F13)Me(py)]	F13	g	[Ni(F13)Me(PPh ₃) ₂]	128
	F14 R ¹ = Me; R ² = CN; R ³ = Me; R ⁴ = <i>i</i> Pr		[Ni ₂ (F14)(η ¹ -CH ₂ Ph)(PMe ₃) ₂]	129 [67]



(continued)

Table 2.1 (continued)

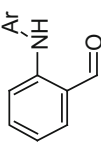
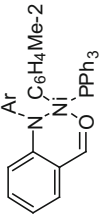
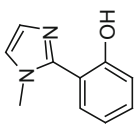
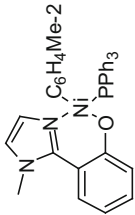
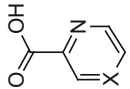
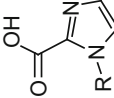
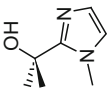
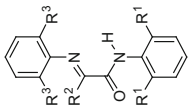
Metal precursor	Ligand	Method	Catalyst	No. References
[NiCl(Ph)(PPh ₃) ₂]	F15 $n = 0$	III	[Ni(F15)(Ph)(PPh ₃)]	130 [68]
	F16 $n = 1$	II	[Ni(F16)(Ph)(PPh ₃)]	131
	F17 $n = 2$		[Ni(F17)(Ph)(PPh ₃)]	132
	F15 $n = 0$	IV'b	[Ni(F15)Me(py)]	133 [68]
	F16 $n = 1$		[Ni(F16)Me(py)]	134
[Ni(py) ₂ Me ₂]	F17 $n = 2$		[Ni(F17)Me(py)]	135
[NiCl(2-MeC ₆ H ₄)(PPh ₃) ₂]				136 [69]
	G1 Ar = 2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂	III	[Ni(G1)(2-MeC ₆ H ₄)(PPh ₃)]	
[NiBr(2-MeC ₆ H ₄)(PPh ₃) ₂]				137 [70]
	G2	II	[Ni(G2)(2-MeC ₆ H ₄)(PPh ₃)]	
<i>5-membered chelated complexes with N-O ligands</i>				
[NiX(2-MeC ₆ H ₄)(PPh ₃) ₂]		III	[Ni(H1)(2-MeC ₆ H ₄)(PPh ₃)]	138 [71]
	H1 X = H			(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiX(2-MeC ₆ H ₄)(P(CH ₂ Ph) ₃) ₂]	H1		[Ni(H1)(2-MeC ₆ H ₄)(P(CH ₂ Ph) ₃)]	139
[NiX(2-MeC ₆ H ₄)(PMePh ₂) ₂]	H1		[Ni(H1)(2-MeC ₆ H ₄)(PMePh ₂)]	140
[NiX(2-MeC ₆ H ₄)(PMe ₂ Ph) ₂]	H1		[Ni(H1)(2-MeC ₆ H ₄)(PMe ₂ Ph)]	141
[NiX(2-MeC ₆ H ₄)(PCy ₃) ₂]	H1		[Ni(H1)(2-MeC ₆ H ₄)(PCy ₃)]	142
[NiX(4-MeC ₆ H ₄)(PPh ₃) ₂]	H1		[Ni(H1)(4-MeC ₆ H ₄)(PPh ₃)]	143
[NiX(Ph)(PPh ₃) ₂]	H1		[Ni(H1)(Ph)(PPh ₃)]	144
[NiX(2,4,6-Me ₃ C ₆ H ₄)(PPh ₃) ₂]	H1		[Ni(H1)(2-MeC ₆ H ₄)(PPh ₃)]	145
[NiX(2-MeC ₆ H ₄)(PPh ₃) ₂]	H2	III	[Ni(H2)(2-MeC ₆ H ₄)(PPh ₃)]	146 [72]
[NiX(2-MeC ₆ H ₄)(PPh ₃) ₂]	H3		[Ni(H3)(2-MeC ₆ H ₄)(PPh ₃)]	147
[NiX(2-MeC ₆ H ₄)(PPh ₃) ₂]	H4		[Ni(H4)(2-MeC ₆ H ₄)(PPh ₃)]	148
	X = C(OMe)			
	X = C(NO ₂)			
	X = N			
				
	H5	III	[Ni(H5)(2-MeC ₆ H ₄)(PPh ₃)]	149 [70]
	H6		[Ni(H6)(2-MeC ₆ H ₄)(PPh ₃)]	150
				

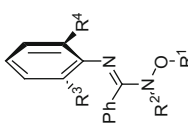
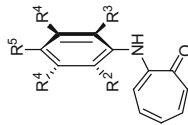
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Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiBr(2-MeC ₆ H ₄)(PPh ₃) ₂]	H7 	II	[Ni(H7)(2-MeC ₆ H ₄)(PPh ₃)]	151 [70]
[Ni(η ¹ -CH ₂ Ph)Cl(PMe ₃) ₂]	I1 R ¹ = R ³ = ⁱ Pr; R ² = Me	III	[Ni(I1)(η ¹ -CH ₂ Ph)(PMe ₃)]	152 [73]
[Ni(η ¹ -CH ₂ Ph)Cl(PMe ₃) ₂]	I2 R ¹ = R ³ = 2- ⁱ Pr,6-Me; R ² = Me	III	[Ni(I2)(η ¹ -CH ₂ Ph)(PMe ₃)]	153 [74]
	I3 R ¹ = R ³ = Et; R ² = Me		[Ni(I3)(η ¹ -CH ₂ Ph)(PMe ₃)]	154
[Ni(η ¹ -CH ₂ Ph)Cl(py) ₂]	I1 R ¹ = R ³ = ⁱ Pr; R ² = Me	III	[Ni(I1)(η ¹ -CH ₂ Ph)(py)]	155 [96]
[Ni(η ¹ -CH ₂ Ph)Cl(2,6-lu) ₂]	I1		[Ni(I1)(η ¹ -CH ₂ Ph)(2,6-lu)]	156
[Ni(η ¹ -C≡OPh)Cl(py) ₂]	I1		[Ni(I1)(η ¹ -C≡OPh)(py)]	157
[Ni(η ¹ -CH ₂ Ph)Cl(PMe ₃) ₂]	I4 R ¹ = R ³ = ⁱ Pr; R ² = Et	III	[Ni(I4)(η ¹ -CH ₂ Ph)(PMe ₃)]	158 [75]
	I5 R ¹ = R ³ = ⁱ Pr; R ² = CH ₂ ⁱ Pr		[Ni(I5)(η ¹ -CH ₂ Ph)(PMe ₃)]	159
	I6 R ¹ = R ³ = R ² = ⁱ Pr		[Ni(I6)(η ¹ -CH ₂ Ph)(PMe ₃)]	160
	I7 R ¹ = R ³ = ⁱ Pr; R ² = Ph		[Ni(I7)(η ¹ -CH ₂ Ph)(PMe ₃)]	161
	I8 R ¹ = R ³ = ⁱ Pr; R ² = 4-CF ₃ C ₆ H ₄		[Ni(I8)(η ¹ -CH ₂ Ph)(PMe ₃)]	162

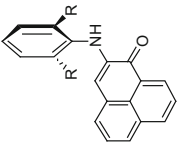
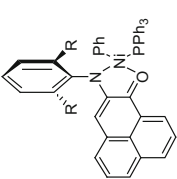
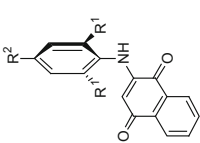
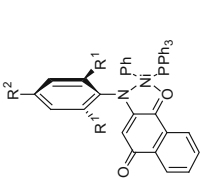
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Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
	I9 $R^1 = R^3 = 'Pr$; $R^2 = 4-MeOC_6H_4$		$[Ni(\mathbf{I9})(\eta^1-CH_2Ph)(PMe_3)]$	163
				
$[Ni(dme)Br_2]$	L1 $R^1 = R^2 = Me$; $R^3 = R^4 = H$	IIa	$[Ni(\mathbf{L1})Br_2]$	164 [76]
	L2 $R^1 = R^2 = R^3 = R^4 = Me$		$[Ni(\mathbf{L2})Br_2]$	165
	L3 $R^1 = R^2 = Me$; $R^3 = R^4 = 'Pr$		$[Ni(\mathbf{L3})Br_2]$	166
	L4 $R^1 = R^2 = Me$; $R^3 = H$; $R^4 = Ph$		$[Ni(\mathbf{L4})Br_2]$	167
				
$[NiCl(Ph)(PPh_3)_2]$	M1 $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = Me$	III	$[Ni(\mathbf{M1})(Ph)(PPh_3)]$	168 [79]
	M2 $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = 'Pr$		$[Ni(\mathbf{M2})(Ph)(PPh_3)]$	169 [78]
	M3 $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = 'Bu$		$[Ni(\mathbf{M3})(Ph)(PPh_3)]$	170 [79]
	M4 $R^1 = R^4 = R^5 = H$; $R^2 = Me$; $R^3 = 'Bu$		$[Ni(\mathbf{M4})(Ph)(PPh_3)]$	171

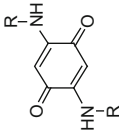
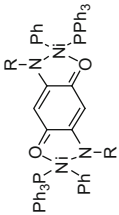
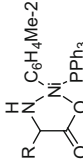
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Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
	M5 $R^1 = R^4 = R^5 = H; R^2 = R^3 = Ph$		[Ni(M5)(Ph)(PPh ₃)]	172
	M6 $R^1 = R^4 = R^5 = H; R^2 = R^3 = Cl$		[Ni(M6)(Ph)(PPh ₃)]	173
	M7 $R^1 = R^4 = R^5 = H; R^2 = R^3 = Br$		[Ni(M7)(Ph)(PPh ₃)]	174
	M8 $R^1 = H; R^2 = R^3 = R^4 = R^5 = F$		[Ni(M8)(Ph)(PPh ₃)]	175
	M9 $R^1 = R^2 = R^3 = R^5 = H; R^4 = CF_3$		[Ni(M9)(Ph)(PPh ₃)]	176
	M10 $R^1 = R^3 = R^4 = R^5 = H; R^2 = Me; R^3 = CF_3$		[Ni(M10)(Ph)(PPh ₃)]	177
	M11 $R^1 = R^4 = R^5 = H; R^2 = Me; R^3 = F$		[Ni(M11)(Ph)(PPh ₃)]	178
	M12 $R^1 = R^4 = R^5 = H; R^2 = R^3 = F$		[Ni(M12)(Ph)(PPh ₃)]	179
	M13 $R^1 = Ph; R^2 = R^3 = 'Pr; R^4 = R^5 = H$		[Ni(M13)(Ph)(PPh ₃)]	180
	M14 $R^1 = 1\text{-naph; } R^2 = R^3 = 'Pr; R^4 = R^5 = H$		[Ni(M14)(Ph)(PPh ₃)]	181
[Ni(M2)Cl(PPh ₃)]	M2 $R^1 = R^4 = R^5 = H; R^2 = R^3 = 'Pr$	h	[Ni(M2)($\eta^1\text{-C}_6\text{H}_{13}$)(PPh ₃)]	182 [107]
				
	N1 $R = Me$	III	[Ni(N1)(Ph)(PPh ₃)]	183 [80]
[NiCl(Ph)(PPh ₃) ₂]	N2 $R = 'Pr$		[Ni(N2)(Ph)(PPh ₃)]	184
				

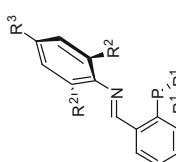
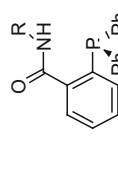
(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[NiCl(Ph)(PPh ₃) ₂]	O1 R ¹ = ⁱ Pr; R ² = H	III	[Ni(O1)(Ph)(PPh ₃)]	185 [81]
[NiCl(Ph)(PPh ₃) ₂]	O2 R ¹ = Me; R ² = H	III	[Ni(O2)(Ph)(PPh ₃)]	186 [82]
	O3 R ¹ = R ² = Me		[Ni(O3)(Ph)(PPh ₃)]	187
	O4 R ¹ = Et; R ² = H		[Ni(O4)(Ph)(PPh ₃)]	188
				
[NiCl(Ph)(PPh ₃) ₂]	P1 R = 2,6- ⁱ Pr ₂ C ₆ H ₃	III	[Ni ₂ (P1)(Ph) ₂ (PPh ₃) ₂]	189 [83]
	P2 R = 2,6-Me ₂ C ₆ H ₃		[Ni ₂ (P2)(Ph) ₂ (PPh ₃) ₂]	190
	P3 R = 1-naph		[Ni ₂ (P3)(Ph) ₂ (PPh ₃) ₂]	191
	P4 R = Ph		[Ni ₂ (P4)(Ph) ₂ (PPh ₃) ₂]	192
	P5 R = Cy		[Ni ₂ (P5)(Ph) ₂ (PPh ₃) ₂]	193
				
[NiBr(2-MeC ₆ H ₄)(PPh ₃) ₂]	Q1 R = H	III	[Ni(Q1)(2-MeC ₆ H ₄)(PPh ₃)]	194 [84]
	Q2 R = ^t Bu		[Ni(Q2)(2-MeC ₆ H ₄)(PPh ₃)]	195
	Q3 R = Ph		[Ni(Q3)(2-MeC ₆ H ₄)(PPh ₃)]	196
	Q4 R = CH ₂ (3-Indolyl)		[Ni(Q4)(2-MeC ₆ H ₄)(PPh ₃)]	197

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
6-membered chelated complexes with N-P ligands				
Pd(OAc) ₂		R ¹ = Ph; R ² = R ³ = H	i	198 [89]
	R ¹ = Ph; R ² = Me; R ³ = H	199		
	R ¹ = Ph; R ² = <i>i</i> Pr; R ³ = H	200		
	R ¹ = 4-MeOC ₆ H ₄ ; R ² = <i>i</i> Pr; R ³ = H	201		
	R ¹ = 3-MeOC ₆ H ₄ ; R ² = <i>i</i> Pr; R ³ = H	202		
	R ¹ = 2-MeOC ₆ H ₄ ; R ² = H; R ³ = Cl	203		
	R ¹ = 2-MeOC ₆ H ₄ ; R ² = H; R ³ = H	204		
	R ¹ = 2-MeOC ₆ H ₄ ; R ² = H; R ³ = OMe	205		
	R ¹ = 2-MeOC ₆ H ₄ ; R ² = <i>i</i> Pr; R ³ = H	206		
[Pd(cod)MeCl]	R ¹ = 2-MeOC ₆ H ₄ ; R ² = <i>i</i> Pr; R ³ = H	IIb		207 [89]

(continued)

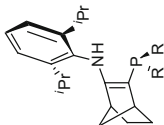
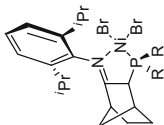
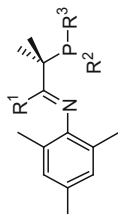
Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
$[\text{Ni}(\eta^1\text{-CH}_2\text{Ph})\text{Cl}(\text{PMe}_3)_2]$	S1 R = Ph	III	$[\text{Ni}(\text{S1})(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)]$	208 [90]
	S2 R = <i>i</i> Bu		$[\text{Ni}(\text{S2})(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)]$	209
	S3 R = H		$[\text{Ni}(\text{S3})(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)]$	210
	S4 R = Pr		$[\text{Ni}(\text{S4})(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)]$	211
	S5 R = <i>i</i> Pr		$[\text{Ni}(\text{S5})(\eta^1\text{-CH}_2\text{Ph})(\text{PMe}_3)]$	212
<i>5-membered chelated complexes with N-P ligands</i>				
$[\text{Ni}(\text{dme})\text{Br}_2]$	T1 Ar = 2,4,6-Me ₃ C ₆ H ₂	IIa	$[\text{Ni}(\text{T1})\text{Br}_2]$	213 [91]
	T2 Ar = 2-MeC ₆ H ₄		$[\text{Ni}(\text{T2})\text{Br}_2]$	214
$[\text{Pd}(\text{cod})\text{MeCl}]$	T1 Ar = 2,4,6-Me ₃ C ₆ H ₂	IIb	$[\text{Pd}(\text{T1})\text{MeCl}]$	215 [91]
	T2 Ar = 2-MeC ₆ H ₄		$[\text{Pd}(\text{T2})\text{MeCl}]$	216

(continued)

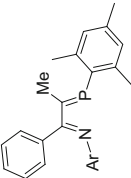
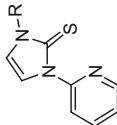
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Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Ni(dme)Br ₂]	U1 	IIa	[Ni(U1)Br ₂] 	217 [34]
[Ni(dme)Br ₂]	U2 R = ^t Bu U3 R = Ph	IIa	[Ni(U2)Br ₂] [Ni(U3)Br ₂]	218 [34] 219
[Pd(cod)Cl ₂]	U1 U2 R = ^t Bu U3 R = Ph	IIa	[Pd(U1)Cl ₂] [Pd(U2)Cl ₂] [Pd(U3)Cl ₂]	220 [34] 221 222
	 V1 R ¹ = Ph; R ² = R ³ = Me V2 R ¹ = R ² = R ³ = Ph V3 R ¹ = H; R ² = Me; R ³ = 2,4,5-Me ₃ C ₆ H ₂ V4 R ¹ = Ph; R ² = Me; R ³ = 2,4,5-Me ₃ C ₆ H ₂ V5 R ¹ = Ph; R ² = R ³ = 2-MeC ₆ H ₄	IIa	[Ni(V1)Br ₂] [Ni(V2)Br ₂] [Ni(V3)Br ₂] [Ni(V4)Br ₂] [Ni(V5)Br ₂]	223 [35] 224 225 226 227
[Pd(cod)MeCl] [Pd(cod)MeCl]	V1 R ¹ = Ph; R ² = R ³ = Me V2 R ¹ = R ² = R ³ = Ph	IIb	[Pd(V1)MeCl] [Pd(V2)MeCl]	228 [35] 229

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
[Pd(cod)MeCl]	V3 R ¹ = H; R ² = Me; R ³ = 2,4,5-Me ₃ C ₆ H ₂		[Pd(V3)MeCl]	230
[Pd(cod)MeCl]	V4 R ¹ = Ph; R ² = Me; R ³ = 2,4,5-Me ₃ C ₆ H ₂		[Pd(V4)MeCl]	231
				
[Pd(cod)MeCl]	W1 Ar = 2,6- ⁱ Pr ₂ C ₆ H ₃			232
	W2 Ar = 2,4,6-Me ₃ C ₆ H ₂	IIb ^j	[Pd(W1)Me(MeCN)][B(C ₆ F ₅) ₄] [Pd(W2)Me(MeCN)][B(C ₆ F ₅) ₄]	233
<i>6-membered chelated complexes with N-S ligands</i>				
				
[Ni(dme)Br ₂]	X1 R = ^t Bu	IIa	[Ni(X1)Br ₂]	234 [93]
	X2 R = 2,6- ⁱ Pr ₂ C ₆ H ₃		[Ni(X2)Br ₂]	235

(continued)

Table 2.1 (continued)

Metal precursor	Ligand	Method	Catalyst	No. References
<i>5-membered chelated complexes with N-S ligands</i>				
[Pd(cod)MeCl]	 Y1	IIb	[Pd(Y1)MeCl]	236 [92]

Abbreviations 9-phen 9-phenanthrenyl; 9-anth 9-anthryl; *m-terp* *m*-terphenyl; *meda* tetramethylethylenediamine; *aacac* acetylacetonate; *dme* dimethoxyethane; *cod* cyclooctadiene; *1-naph* 1-naphthyl; *tppts* tri(*m*-sulfonylphenyl)phosphine; *tpnds* di(*m*-sulfonylphenyl)phenylphosphine; *H₂N-PEG-OMe*, amino-terminated poly(ethylene glycol) monomethoxy ether; *pta* 1,3,5-triaza-7-phosphaadamantane; *hmta* hexamethylenetetramine; *dms* dimethylsulfoxide; 2,6-*lu* 2,6-lutidine

^aUnspecified mechanism

^bMultiple ligand exchange

^cIn situ alkylation with MeLi

^dCod displacement followed by oxidative addition

^eReaction with NaH(OMe)₃

^fFrom catalytic process involving: (i) E insertion in Ni-Me; (ii) β-H elimination with propylene releasing and Ni-H formation; (iii) insertion of E into Ni-H bond

^gLigand exchange between py and PPh₃

^hAlkylation with *n*-hexyl magnesium bromide

ⁱIn situ generation of catalyst by addition of TsOH probably involving oxidative addition

^jFollowed by reaction with NaB (C₆F₅)₄

The novelty and the interest in these Ni and Pd complexes with mixed N–O, N–P, and N–S chelating ligands resides in that most bear anionic ligands and thus catalysts are neutral. They include primarily alkyl and aryl nickel complexes with salicylaldimine, anilino tropone, enolatoimine derivatives, and others developed afterwards. Besides the hydrocarbyl ligands, which effectively trigger the polymerization, they are also characterized by the presence of bulky groups on the ancillary ligand, and a neutral monodentate ligand such as PR_3 or more labile ligands, such as MeCN, pyridine, lutidine, etc. Their activation requires the removal of the neutral ligand (L) to form the coordination vacancy for the incoming olefin. Depending on the relative binding strength of L to the metal center the activation can require or not a scavenger, such as $[\text{Ni}(\text{cod})_2]$ or $\text{B}(\text{C}_6\text{F}_5)_3$. The strength of the interaction is connected with structural and electronic features of the complex as well as with steric and electronic properties of L.

Relating to Ni-salicylaldimine (Fig. 2.21) the need to use a scavenger to extract L can be avoided by selective introduction of bulky groups in *ortho*-position (R^1) to O-donor, by introducing EWGs in *para*-position (R^2) to O-donor, and by using more labile L such as py or MeCN. All these modifications on original catalyst skeleton promote activation by simple thermal dissociation by decreasing the strength of phosphine-nickel bond.

Fig. 2.20 Activation by aluminium-based cocatalysts

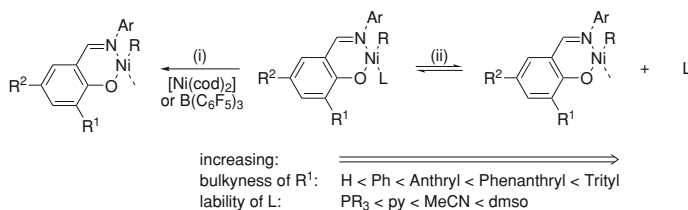
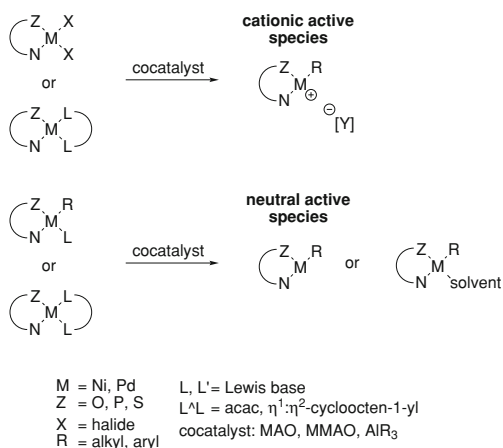


Fig. 2.21 Examples of the effect of ligands on activation of salicylaldiminato Ni complexes

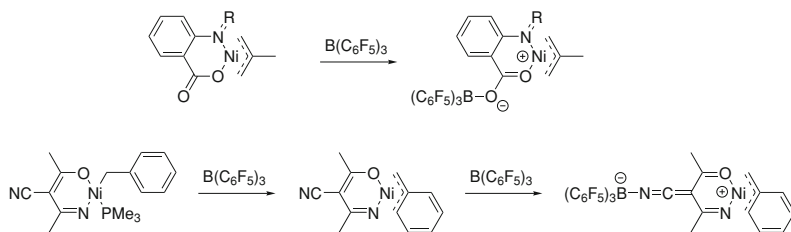


Fig. 2.22 Examples of remote activation generating zwitterionic catalysts

Interestingly, what influences activation has also a strong impact on the whole catalytic process. Indeed, the decreasing energy in Ni–L bond is effective also in intermediates involved in propagation, such as metal-growing chain and hydrido species, demonstrated to be resting states. Moreover, the presence of a bulky group in R^1 position prevents the formation of bischelate complexes $[\text{Ni}(\kappa^2\text{-N,O})_2]$, recognized as deactivation route for these systems.

Differently, anilintropone- and anilinoperinaphtenone-based systems with the strong σ -donor PPh_3 and a scaffold without EWGs or particularly bulky substituents act as single component catalysts. The easy removal of the phosphine donor can be explained in terms of trans-influence of amido ligand. Nevertheless, *ortho*-aryl effect has an influence on productivity, catalyst lifetime, and polymer properties also in these systems.

Similarly, the family of complexes with enolatoimine ligands behave as single component catalysts thanks to the highly negative nitrogen, which enhances the rate of dissociation of phosphine or pyridine. As a general rule, the substitution of phosphine with more labile ligands, such as pyridine or lutidine ligands prevents the use of activators. This is true for a variety of catalysts including diazene- and α -iminocarboxamide-based systems.

A novel activation concept, sometimes referred as remote activation, was reported in the frame of zwitterionic catalysts. This type of activation places the Lewis acid away from the trajectory of monomer insertion and eliminates the complexities associated with the use of MAO derivatives and the equilibria of complexes where anion decoordination or displacement required for monomer insertion. Essentially, remote activation requires a ligand with an available basic functionality for the Lewis acid attachment, often a carbonyl group, which acts as an electronically delocalized canal towards the metal center. Generation of zwitterionic species is often accomplished by reorganization of the coordination sphere surrounding the metal. Examples of this activation are reported in Fig. 2.22 for iminobenzoato- and ketoimino-based ligands containing catalysts **108** and **128**.

2.4.2 Ethylene Polymerization

The development of electron-rich catalyst systems compatible with polar functionality would satisfy the desire to include polar functionalities into linear

(Fig. 2.23) polyolefins with precise control over polymer characteristics such as mechanical toughness, rheology, and surface functionalization properties, as well as avoid the need for rigorous drying of monomers and polymerization solvents. Such interest turned the attention towards the cationic (N–N) group 10 systems pioneered by Brookhart and to cationic and neutrally charged (N–Z) group 10 systems reviewed in this chapter. The need to reach a rational design of catalysts which allows to control activity, molar masses, and branching, in addition to tolerance to functional groups led to much research studies on α -olefin polymerization pioneered by Grubbs [38] and Johnson [85]. New families of complexes were introduced, the main results in ethylene polymerization are reviewed following the ligand organization in Fig. 2.1. Selected polymerization data of the main (N–Z)Ni catalysts are reported in Table 2.2.

Independently Grubbs at Caltech [38] and Johnson at Dupont [85] rationalized to replace the P–O chelate of the neutral SHOP system [24] with a ligand based on the harder nitrogen and a scaffold containing increased steric demand to have polymers with high molecular weight; both selected salicylaldimine complexes. The DuPont group reported use of allyl complexes, while the Caltech group used the phosphine complexes. Grubbs reported that neutral Ni(II) salicylaldiminato complexes are highly active catalysts for the polymerization of ethylene to high molecular weight polymers under moderate conditions [38]. The introduction of bulkier substituents on the imine nitrogen and the phenolic ring blocks the axial faces of the metal center, retarding the rate of associative displacement (Fig. 2.23). Moreover, bulky groups might decrease the rate of catalyst deactivation, which was shown to occur by ligand disproportionation and dimerization as in the analogous SHOP system.

The polymerization of ethylene by complexes 1–7 were performed in toluene by injection of a toluene solution of the appropriate phosphine scavenger ($[\text{Ni}(\text{cod})_2]$ or $\text{B}(\text{C}_6\text{F}_5)_3$) to the catalyst solution. Attempts to polymerize ethylene without the phosphine scavenger did not yield polyethylene [38]. However, when the catalyst 1 was combined with a phosphine scavenger, after a 5–8 min induction period, there was a rapid ethylene uptake. Increasing the ethylene pressure yields polyethylene with higher M_w . Bulky substituents in the *ortho*-position to O donor suppress the chain migratory process and also the chain termination reactions. In fact, catalysts 2–5 produced higher molecular weight than 1 and a slight decrease of total number of branches. Moreover, no induction period was observed. Best results were obtained with an electron deficient system (7), bearing the NO_2 substituent in *p*-position to O donor (R^2) of the salicylaldiminato, while catalyst

Fig. 2.23 Examples of the effect of substituent variation in salicylaldiminato catalysts

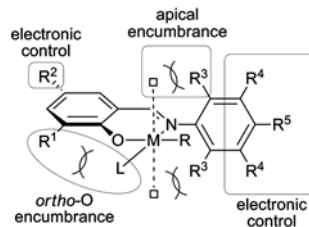
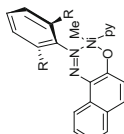
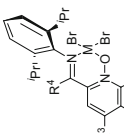
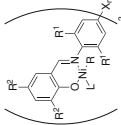
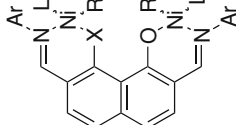
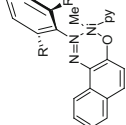


Table 2.2 continued

6-membered chelated complexes with N–O ligands													
R ¹	R ²	R ³	R ⁴	R ⁵	L	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ^{−1})	M _w /M _n	Br/1000 C	References
	9-anth	H	3,5-'Bu ₂ -4-OHC ₆ H ₂	H	Py	38	40	50	1,242	44.8	2.8	30	[48]
	9-anth	H	3,5-Me ₂ C ₆ H ₃	H	Py	39	40	50	1,374	12.5	3.9	92	[48]
	9-anth	H	3,5-Me ₂ -4-MeOC ₆ H ₂	H	Py	40	40	50	707	2.4	2.7	88	[48]
	9-anth	H	3,5-(MeO) ₂ C ₆ H ₃	H	Py	41	40	50	538	17.2	4.3	80	[48]
	9-anth	H	3,4,5-(MeO) ₃ C ₆ H ₂	H	Py	42	40	50	641	53.0	5.3	78	[48]
H	NO ₂	3,5-(CF ₃) ₂ C ₆ H ₃	H	H	Py	43	40	50	750	20.4	2.4	15	[48]
^t Bu	H	3,5-(CF ₃) ₂ C ₆ H ₃	H	H	Py	44	40	50	100	21.1	2.2	14	[48]
6-membered chelated complexes with N–O ligands													
R ¹	R ²	R ³	R ⁴	L	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ^{−1})	M _w /M _n	Br/1000 C	References	
	H	H	Me	–	73 /MMAO	5	30	556	3.0	1.7	87	[53]	
	H	H	H	–	74 /MMAO	5	30	836	1.7	1.7	65	[53]	
	Ph	H	H	–	76 /MMAO	5	30	3,084	57.2	2.8	30	[53]	
	H	H	MeO	H	–	78 /MMAO	5	30	476	2.8	1.2	70	[53]
cyclohexylidene	–	–	–	η ³ -CH ₂ CMeCH ₂	108	3.4	50	1,700	7.3	2.0	43	[61]	
CEt ₂	–	–	–	η ³ -CH ₂ Ph	110	5.2	50	4,100	12.0	2.3	47	[61]	

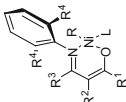
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Table 2.2 continued

6-membered chelated complexes with N-O ligands													
R ¹	R ²	R ³	R ⁴	L	Cat. no.	pE (bar)	T (°C)	TOF _a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1,000 C	References	
	n = 0; ⁱ Pr	I	I	-	py	92	40	50	770	381.6	5.3	4	[56]
	n = 0; 3,5-(CF ₃) ₂ C ₆ H ₃	I	I	-	py	93	40	50	3,400	236.8	3.2	4	[56]
	n = 1; X = CH ₂ ; ⁱ Pr	I	I	-	py	94	40	50	480	437.0	4.6	4	[56]
	n = 1; X = CH ₂ ; 3,5-(CF ₃) ₂ C ₆ H ₃	I	I	-	py	95	40	50	5,040	249.0	3.0	4	[56]
	n = 0; 3,5-(CF ₃) ₂ C ₆ H ₃	I	I	-	tmeda	96	40	50	9,520	920	3.3	2	[56]
	X = O	-	-	-	PMe ₃	104/ ^{Ni(cod)₂}	7	25	99	10.3	2.6	80	[60]
	X = O	-	-	-	PPh ₃	106/ ^{Ni(cod)₂}	7	25	102	10.1	2.6	93	[60]
6-membered chelated complexes with N-O ligands													
R ¹	R ²	R ³	R ⁴	R ⁵	L	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1000 C	References
/	/	ⁱ Pr	H	H	py	113	50	70	80	52.0	1.9	-	[62]
													

(continued)

Table 2.2 continued

6-membered chelated complexes with N-O ligands													
R ¹	R ²	R ³	R ⁴	R ⁵	L	Cat. no.	pE (bar)	T(°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w / M _n	Br/1000 C	References
	CF ₃	COCF ₃	H	ⁱ Pr	-	PPh ₃ 117	13.78	60	14,168	25.0	3.7	41	[64]
	CF ₃	COCF ₃	Me	ⁱ Pr	-	PPh ₃ 118	13.78	50	2,968	27.0	3.3	58	[64]
	CF ₃	H	Me	ⁱ Pr	-	PPh ₃ 119	13.78	50	896	17.0	-	-	[64]
	Ph	H	H	ⁱ Pr	-	PPh ₃ 121/ B(C ₆ F ₅) ₃	25	60	345	27.3	2.2	25	[65]
2-PhC ₆ H ₄	H	H	ⁱ Pr	-	PPh ₃ 122/ B(C ₆ F ₅) ₃	25	25	60	3,420	17.0	1.8	22	[65]
2-Naph- C ₆ H ₄	H	H	ⁱ Pr	-	PPh ₃ 123/ B(C ₆ F ₅) ₃	25	25	60	2,625	9.0	2.0	39	[65]
CF ₃	COCF ₃	H	ⁱ Pr	-	py 126	40	40	60	3,864	24.0	3.0	-	[66]
CF ₃	COCF ₃	H	3,5-(CF ₃) ₂ C ₆ H ₃	-	py 127	40	40	60	687	38.0	2.3	-	[66]
CF ₃	COCF ₃	H	3,5-(CF ₃) ₂ C ₆ H ₃	-	PPh ₃ 128	40	40	70	2,280	32.0	2.1	-	[66]
CF ₃	COCF ₃	H	3,5-(CF ₃) ₂ C ₆ H ₃	-	PPh ₃ 128/Ni(cod) ₂	40	40	70/100	4,680	21.0	5.1	-	[66]
n = 0	-	-	-	-	PPh ₃ 130	50	50	63	1,760	9.8	1.9	54	[68]
n = 1	-	-	-	-	PPh ₃ 131	50	50	63	1,875	46.8	2.0	26	[68]
n = 2	-	-	-	-	PPh ₃ 132	50	50	63	3,570	46.5	2.1	27	[68]
n = 0	-	-	-	-	py 133	25	25	63	1,005	8.2	2.1	77	[68]
n = 1	-	-	-	-	py 134	50	50	63	1,791	56.9	1.9	28	[68]
n = 2	-	-	-	-	py 135	25	25	63	960	41.6	2.1	47	[68]

(continued)

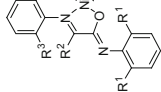
Table 2.2 (continued)

5-membered chelated complexes with N–O ligands												
R ¹	R ²	R ³	R	L	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kgmol ^{−1})	M _w /M _n	Br/1000 C	References
ⁱ Pr	Me	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	152/B (C ₆ F ₅) ₃	6.89	20	350	349.0	2.3	104	[73]
ⁱ Pr	Me	ⁱ Pr	η^1 -CH ₂ Ph	Py	155	6.89	20	60	63.0	1.8	–	[96]
ⁱ Pr	Me	ⁱ Pr	η^1 -CH ₂ Ph	2,6-lu	156	6.89	40	304	143.0	2.2	–	[96]
ⁱ Pr	Me	ⁱ Pr	η^1 -C=OPh	Py	157	27.57	50	301	160.0	2.0	–	[96]
ⁱ Pr	Et	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	158/Ni (cod) ₂	6.89	20	255	111.8	1.3	–	[75]
ⁱ Pr	CH ₂ ⁱ Pr	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	159/Ni (cod) ₂	6.89	20	420	169.4	1.4	–	[75]
ⁱ Pr	ⁱ Pr	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	160/Ni (cod) ₂	6.89	20	534	218.4	1.2	–	[75]
ⁱ Pr	Ph	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	161/Ni (cod) ₂	6.89	20	259	122.4	1.2	–	[75]
ⁱ Pr	4-CF ₃ C ₆ H ₄	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	162/Ni (cod) ₂	6.89	20	280	124.3	1.1	–	[75]
ⁱ Pr	4-MeOC ₆ H ₄	ⁱ Pr	η^1 -CH ₂ Ph	PMe ₃	163/Ni (cod) ₂	6.89	20	180	109.2	1.2	–	[75]

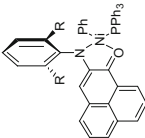
R ¹	R ²	R ³	R ⁴	R ⁵	No.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ^{−1})	M _w /M _n	Br /1000 C	References
H	Me	Me	H	H	168	13.78	80	5,424 ^b	73.1	1.7	61	[79]
H	ⁱ Pr	ⁱ Pr	H	H	169	13.78	80	8,800 ^b	165.6	1.8	61	[79]
H	Me	ⁱ Bu	H	H	171	13.78	80	1,014 ^b	230.0	2.0	73	[79]
H	Ph	Ph	H	H	172	13.78	80	10,038 ^b	171.0	1.8	53	[79]
H	Cl	Cl	H	H	173	13.78	80	3,924 ^b	20.0	2.0	53	[79]
H	Br	Br	H	H	174	13.78	80	4,152 ^b	41.8	1.9	56	[79]

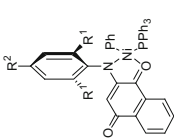
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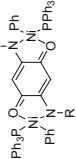
Table 2.2 (continued)

	R ¹	R ²	R ³	R ⁴	R ⁵	No.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1000 C	References
	H	F	F	F	F	175	13.78	80	1,152 ^b	4.8	3.0	49	[79]
	H	Me	H	H	H	176	13.78	80	936 ^b	112.8	2.4	57	[79]
	H	Me	CF ₃	H	H	178	13.78	80	6,924 ^b	167.2	1.9	59	[79]
	Ph	ⁱ Pr	ⁱ Pr	H	H	180	13.78	80	2,338	184.8	2.1	63	[79]
	1-Naph	ⁱ Pr	ⁱ Pr	H	H	181	13.78	80	2,461	151.2	2.7	62	[79]

5-membered chelated complexes with N–O ligands

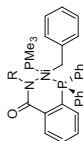
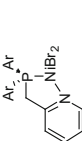
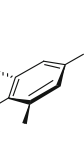
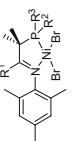
	R ¹	R ²	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1000 C	References
	ⁱ Pr	/	184	13.78	80	1,749	144.0	1.6	44	[80]

	R ¹	R ²	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1000 C	References
	ⁱ Pr	H	185	1.01	40	1,460	150.9	3.3	22	[81]
	Me	H	186	1.01	40	363	11.4	2.2	41	[82]
	Me	H	186	1.01	20	39	105.0	2.2	5	[82]
	Me	Me	187	1.01	20	176	255.0	2.4	9	[82]
	Et	H	188	1.01	40	394	185.6	2.0	12	[82]

	R ¹	R ²	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ⁻¹)	M _w /M _n	Br/1000 C	References
	2,6- ⁱ PrC ₆ H ₃	–	189	4	40	104	43.1	3.5	–	[82]
	2,6-MeC ₆ H ₃	–	190	4	80	64	53.5	8.2	–	[83]

(continued)

Table 2.2 (continued)

5-membered chelated complexes with N–O ligands										
R ¹	R ²	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ^{−1})	M _w /M _n	Br/1000 C	References	
	H	194	40	100	1,756	900.0	–	1.8	[84]	
6-membered chelated complexes with N–P ligands										
R ¹	R ²	R ³	Cat. no.	pE (bar)	T (°C)	TOF ^a	M _w (kg mol ^{−1})	M _w /M _n	Br/1000 C	References
	–	–	212	6.89	50	5,300	1,070.0	3.7	60	[90]
	2,4,6-Me ₃ C ₆ H ₂	–	213/MAO	34.47	30	15	9.2	2.1	76	[91]
	Ph	Me	223/MMAO-3A	27.57	35	1,000	2.8	–	66	[35]
	Ph	Ph	224/MMAO-3A	27.57	29	667	140.0	1.9	64	[35]
	H	Me	225/MMAO-3A	27.57	60	960	37.0	n.d.	57	[35]
	Ph	2-MeC ₆ H ₄	226/MMAO-3A	27.57	29	1,386	75.0	1.8	67	[35]

^a Kg PE mol cat^{−1} h^{−1}^b Polymerization time = 10 min

activity diminishes with electron rich catalyst such as **6**. However, complex **7**, with greatest activity, gave a broad molecular weight distribution ($M_w/M_n > 12.4$) [38]. Salicylaldimines with sufficient bulk in the *ortho*-position to O donor constitute a new family of neutral, single component catalysts [39]. In the absence of cocatalysts, catalysts **3–5** have an indefinite lifetime and are capable of producing TOFs from 0.5×10^3 to 3.0×10^3 kg PE mol Ni⁻¹ h⁻¹ at low temperatures and pressures. Grubbs did not observe a dissociated phosphine in NMR spectroscopic studies of the polymerization reaction suggesting that the resting state of these systems is the phosphine complex. Activity of the catalysts containing phosphine was reduced by additional amounts of phosphine and increased with temperature up to 80 °C.

In order to further enhance the activity of the catalyst, Grubbs et al. [39] prepared complexes containing the acetonitrile ligand, more labile than triphenylphosphine. This family of catalysts (**8–10**) exhibits a 2- to 3-fold increase in catalytic activity as compared with catalysts **3–5**. Complexes **13–16**, easily prepared from readily available Ni complexes and salts, were synthesized by Chen [41] and activated by near-stoichiometric amounts of almost any metal-alkyl or hydride (BuLi, MAO, BH₃·THF, or MeLi) for the polymerization of ethylene (at 1–75 bars of ethylene). Catalyst productivity was found to depend on ethylene pressure and similar for all three complexes with all the activators except for complex **13** that shows at $pE = 75$ bar a turnover number (TON = mol PE mol Ni⁻¹) of over 10⁵. The catalyst showed a long lifetime and the polymer produced was highly linear.

Carlini et al. [42] reported the synthesis of monochelate nickel (II) catalysts **17–20**, obtained by in situ oxidative addition of salicylaldimine ligands to [Ni(cod)₂], for the polymerization of ethylene. Almost stoichiometric amounts of MAO as cocatalyst are necessary to activate these systems, the productivity being dependent on the Al/Ni molar ratio. Both activity and molecular weight of the resulting PE are influenced by the nature of the substituent on both the phenolate moiety and on the N-aryl ring. In particular, when two nitro groups are present on the 3,5-positions of phenolate moiety (**19**, **20**) activities are higher than 120 (kg PE mol Ni⁻¹ h⁻¹). The PE obtained showed a high linearity and M_w was in the 100–500 kg mol⁻¹ range.

Further studies on the effect of free trimethylaluminum (TMA) content in MAO on performances of catalyst **19** [43] led to conclude that TMA alone is not able to activate the catalyst in the polymerization of ethylene and MAO appears necessary. When a large excess of TMA with respect to the amount of catalyst was used, independently of the relative amount of MAO and hence of the Al_{tot}/Ni molar ratio, a significant detrimental effect on both the activity and PE molecular weight was generally obtained. For TMA/Ni molar ratio = 15 high molecular weight linear PE was obtained with the maximum of activity (1,920 kg PE mol Ni⁻¹ h⁻¹) when a proper amount of MAO was also present (Al_{tot}/Ni = 150).

The interest in the synthesis of latexes of high-molecular-weight polyethylene prompted Mecking et al. to design novel Ni(II) salicylaldiminato complexes. Based on the interesting results with **11** they reasoned that an R³ aryl substituent

with strongly electron-withdrawing groups could provide steric bulk and electron withdrawing properties at the same time [44]. A series of salicylaldimine ligands with systematically varied electronic properties were synthesized and employed as precursors for ethylene polymerization (**21–25**). They are characterized from having a nickel bound methyl group in the trans position to the O donor, a pyridine as labile ligand, and a strong steric shielding of the apical positions of the metal center by the R^3 aryl groups of the N-aryl moiety. This series of well-defined catalyst precursors with a systematically varied substitution pattern revealed a surprising and unprecedented effect of remote substituents on polymer branching and molecular weight, despite their spatial remoteness from the catalytically active center.

Performances of complexes **21–25** were compared with those of complex **12**. The activity of all catalysts with 3,5-substituted aryl moieties ($R^3 = 3,5-(CF_3)_2C_6H_3$ (**21**), $3,5-(Me)_2C_6H_3$ (**24**) and $3,5-(OMe)_2C_6H_3$ (**25**)) is much higher than that of **12** with the isopropyl substitution pattern. Catalysts which do not bear substituents in the 3,5-position ($R^3 = Ph$ (**23**)) or are only monosubstituted ($R^3 = 3-NO_2C_6H_4$ (**22**)) appeared much less active. Studies of catalyst stability over time revealed that **21**, **24**, **25**, and **12** remain active for hours at 60 °C and 10 bar ethylene pressure, **22** and **23** are deactivated completely within 20 min.

Surprisingly, despite their spatial distance from the metal center the nature of the substituents on the aryl moiety has a dramatic effect on branching and thus crystallinity, and on polymer molecular weight. With $R^3 = 3,5-(CF_3)_2C_6H_3$ (**21**) a semicrystalline (50% crystalline) stiff polymer was obtained. Complexes with $R^3 = 3-NO_2C_6H_4$ (**22**) and $R^3 = 3,5-(CF_3)_2C_6H_3$ (**21**) afford polyethylenes with a considerably higher degree of branching, and correspondingly low crystallinities (18 and < 10%, respectively), and from those with $R^3 = 3,5-(Me)_2C_6H_3$ (**24**) and $R^3 = 3,5-(OMe)_2C_6H_3$ (**25**) an entirely amorphous material is obtained. At the same time, the molecular weight of the polymer decreases by more than an order of magnitude going from **21** to **25**. Given the similar intrinsic activities of all catalysts, the lower molecular weight obtained must indeed result from a higher rate of chain transfer rather than from a lower rate of chain growth.

The methyl branching originates from a β -H transfer and a subsequent 2,1-reinsertion of the resulting metal-bound 1-olefin. Whereas the steric requirements of the substituents are similar in **21**, **24** and **25** ($R^3 = 3,5-(CF_3)_2C_6H_3$ (**21**), $R^3 = 3,5-(Me)_2C_6H_3$ (**24**), and $R^3 = 3,5-(OMe)_2C_6H_3$ (**25**)) and higher than in **23** ($R^3 = C_6H_5$), their electron withdrawing character increases in the sequence **25** ~ **24** < **23** < **22** ~ **21**. Both the molecular weights and the branching of the polymers obtained with these different catalyst precursors vary systematically with the electronic nature of R rather than their steric requirements. This indicates that the effect of these remote substituents is related to their electronic properties.

Catalytic performances of complexes **21**, **24**, and **25** were compared to those of two other series of (κ^2 -N,O)-salicylaldiminato Ni(II)-methyl pyridine complexes **33–35** and **36–42** [48], the former have two iodine substituents in *ortho*- and *para*-positions of the phenolate moiety, the latter and **32** have an anthryl substituent in *ortho* and triphenyl with different substitutions in 3 and 5 ($R^3 = 3,5-(CF_3)_2C_6H_3$

(**36**), $R^3 = 3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$ (**37**), $R^3 = 3,5\text{-}^t\text{Bu}_2\text{-4-OHC}_6\text{H}_2$ (**38**) etc.) [47]. All behave as single component ethylene polymerization catalysts at temperatures above 15 °C, reaching their highest productivities in the range between 40 and 75 °C. The anthryl-substituted complex **37** is the most active precatalyst under these polymerization conditions (1,860 kg PE mol Ni^{-1} h $^{-1}$), while all diiodo-substituted complexes **21**, **24**, **25**, and **33–35** perform similarly well when compared to the respective anthryl-substituted complexes **32**, **36–42**. Further, the anthryl versus diiodo substitution does not exert a major influence on the degree of branching of the obtained polyethylenes.

As already found for complexes **21**, **24**, and **25**, [44] the degree of branching of obtained polyethylenes is highly sensitive to the 3,5-substitution pattern of the terminal arene rings of the terphenyl moieties in both diiodo- and anthryl-substituted complexes. More electron-deficient N-aryl substituents result in higher molecular weights and lower degrees of branching probably by suppressing chain walking and chain transfer relative to ethylene insertion.

At 50 °C all catalysts are quite stable. In more detail, complexes **32**, **21**, and **44** derived from 2,6-diisopropylaniline or terphenylamine appeared to exhibit constant polymerization activities over time and polymer yields in 40 and 60 min (for **21**: 120 min) polymerization runs. Further, complexes **33**, **34**, **37**, and **38** showed a slight decrease in polymerization activity over time reaching one-half of the initial activity after ca. 1.5–2.0 h, while one-half of the initial activities after ca. 1 h were observed with complexes **24**, **25**, **39**, and **43**. At 70 °C, the decrease in polymerization activities over time is more pronounced with precatalysts **37** and **38**. It was concluded that the positive effect on the stability of the anthryl substituent in **5** observed by Grubbs [38] is not valid when anthryl and terphenyl substituents are combined in the same catalyst. Probably deactivation mechanisms are different.

Moreover, Mecking [49] synthesized another series of (k^2 -N,*O*)salicylaldiminato nickel methyl pyridine complexes as precatalysts varying the remote substituents of 2,6-di-(4-*R*-phenyl)phenyl groups on the imine nitrogen [$R = \text{C}_8\text{F}_{17}$ (**28**), CF_3 (**29**), F (**48**), H (**23**), Me (**46**), ^tBu (**48**), OMe (**47**), and NMe_2 (**49**)] to complete the studies on the electronic effects of remote substituents.

Also these complexes behave as single component catalysts but catalyze the polymerization of ethylene to low molecular weight polyethylene. Decreasing molecular weight and increasing degrees of branching are observed in the order $R = \text{C}_8\text{F}_{17} \sim \text{CF}_3 > \text{F} > \text{H} > \text{Me} > \text{MeO} > ^t\text{Bu} > \text{NMe}_2$. They are less active and decompose faster, under the polymerization conditions employed, than complexes 2,6-di-(3,5- R'_2 -phenyl)phenyl substituted. X-ray diffraction analysis of complex **45** ($R^2 = \text{I}$; $R^3 = 4\text{-FC}_6\text{H}_4$) and polymerization results indicated that it is not the sterics but the electronics of the R' group that controls the polymer microstructure.

The cyclohexyl-substituted salicylaldiminato-Ni(II) complex **26** was tested by Sun et al. [45] in the ethylene polymerization. As a single component catalyst, complex **26** shows no activity in the polymerization of ethylene. Then, $[\text{Ni}(\text{cod})_2]$ was used as cocatalyst to trap the triphenylphosphine. The catalytic activity of **26** and the molecular weight of PE are in relation to the amount of $[\text{Ni}(\text{cod})_2]$ added

as a cocatalyst. The catalytic activity increases as the $[\text{Ni}(\text{cod})_2]/\mathbf{26}$ molar ratio increases and 3 or 4 equiv. of the cocatalyst are sufficient for the whole polymerization time. The activity increases with increasing temperature during the initial stage and reaches the maximum values at 45–55 °C. A polymerization activity of $3.62 \times 10^2 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$ and a M_n of 57.3 kg mol^{-1} have been found for 10 μmol of **26** and a $[\text{Ni}(\text{cod})_2]/\mathbf{26}$ ratio of 3 at 45 °C and 12 bar of ethylene. The polydispersity index of the resulting polyethylene is 2.04. Moreover, the aluminum alkyls AlEt_3 and Al^iBu_3 were tested as cocatalyst. The activity of the catalyst and M_n of PE are lower than those produced with $[\text{Ni}(\text{cod})_2]$.

There is an increasing interest in the field of single-site bimetallic olefin polymerization catalysis since these systems may exhibit increased activity, branch formation, and comonomer enchainment versus their mononuclear analogues. The origin of these bimetallic cooperativity effects is proposed to include non-negligible comonomer secondary binding to weakly basic groups on the olefin which modifies relative chain transfer rates and facilitates comonomer enchainment at the second, proximate metal center.

The first example of neutral binuclear nickel(II) catalysts are the bimetallic salicylaldimine–nickel complexes with *tert*-butyl (**80**) or Ph (**81**) substituents in R^2 were prepared by Zhang [54]. At 10 atm of ethylene pressure complex **80** was catalytically less active toward ethylene polymerization with ca. 2–3 equiv. of $[\text{Ni}(\text{cod})_2]$ as phosphine scavenging agent, while complex **81** comprising a phenyl group was demonstrated to have high potential for ethylene polymerization without any cocatalyst. Although *t*-Bu groups are generally considered to be bulkier than unsubstituted phenyl group, phenyl is more electron-withdrawing than *t*-Bu. Complex **81** ($\text{R}^2 = \text{Ph}$), therefore, revealed a marked increase from 37 kg PE mol $\text{Ni}^{-1} \text{ h}^{-1}$ for **80** ($\text{R}^2 = t\text{-Bu}$) to 110 kg PE mol $\text{Ni}^{-1} \text{ h}^{-1}$. This electron-deficient effect is consistent with the electronic effect of mononuclear Grubbs catalysts. It is notable that the polymerization temperature greatly influences the activity of the binuclear nickel catalyst. For **81**, lower temperature (30 °C) represents the optimum and at an increased temperature of 50 °C or 70 °C, catalytic performance quickly decreased from 290 kg PE mol $\text{Ni}^{-1} \text{ h}^{-1}$ to be 64 and 21 kg PE mol $\text{Ni}^{-1} \text{ h}^{-1}$, respectively.

Polyethylene obtained employing binuclear **81** revealed higher $M_w = 141 \text{ kg mol}^{-1}$ and relatively broader molecular weight distribution ($M_w/M_n = 6.1$) than PE from the mononuclear one ($M_w = 18.6 \text{ kg mol}^{-1}$, $M_w/M_n = 2.8$). The broad polydispersity was supposed to arise from the interactions of the metal centers, electronically coupled through the ligand, which may create more than one active species. ^{13}C NMR showed that the polymers produced by **81** are moderately branched, with methyl branches predominating (ca. 20 methyl branches per 1,000 carbon atoms).

High catalytic activities for ethylene polymerization with a series of novel *m*-arene-bridged salicylaldimine-based binuclear neutral nickel(II) complexes (**82–91**) in the presence or absence of the phosphine scavenger $[\text{Ni}(\text{cod})_2]$ were also obtained by Huang et al. [55]. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly.

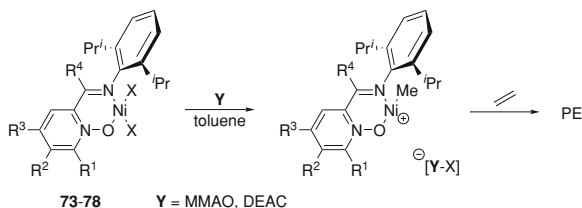
Highly branched polyethylenes (46–127 branches per 1,000 carbon atoms) with moderate molecular weights ($M_n = 10\text{--}169\text{ kg mol}^{-1}$) and narrow molecular weight distributions ($M_w/M_n = 2.3\text{--}2.4$) were obtained. In the presence of a polar solvent such as THF or Et_2O , complex **89** polymerizes ethylene as a single-component catalyst. The variation of substituents on the *ortho*-positions of the phenyl rings and arene bridge of the ligand dramatically influences the polymerization behavior of these binuclear nickel complexes. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly, and very high molecular weight polyethylenes can be obtained by complexes **90** and **91** with nitro groups. In comparison to the corresponding mononuclear Ni catalysts, the binuclear Ni catalysts showed higher thermal stability, and complexes **82**, **84**, **86**, and **87**, which feature small R^2 substituents, are capable of acting as single-component ethylene polymerization catalysts showing much higher thermal stability and can tolerate polar functional groups.

Recently, novel binuclear Ni(II) methylpyridine complexes (**92–95**) of di(salicylaldimines) bridged in the *p*-position of the N-aryl moiety were prepared and characterized by Mecking [56], and studied for ethylene polymerization. No activators were used with the pyridine complexes. They are active between 20 and 70 °C as single-component catalyst precursors. Maximum productivities were observed at 50 °C, while at higher temperatures some deactivation occurs. Mecking compared the performances of pyridine complexes to those of the complex with the less strongly coordinating tertiary amine tmeda (**96**). A high activity was observed at low polymerization temperature (20 °C). In both cases the substitution in the 2, 2', 6, and 6' positions of the N-aryl moieties with 3,5-bis(trifluoromethyl)phenyl groups results in more active catalysts than isopropyl substitution.

Polymerization activities of all binuclear complexes are substantially higher than those of mononuclear analogues. A maximum activity of $9,520\text{ kg PE mol Ni}^{-1}\text{ h}^{-1}$ was observed for **96**, with formation of high molecular weight polymers of $M_w\ 920\text{ kg mol}^{-1}$ and $M_n\ 280\text{ kg mol}^{-1}$. The increase in polymerization activity of the binuclear complexes, compared to the mononuclear analogues, appears to be due to an intrinsically higher rate of chain growth rather than to a more efficient dissociation of pyridine as activator of the catalyst precursors. Polymer microstructure is affected by chain walking only to a small extent. Linear polyethylenes with, for example, two methyl branches per 1,000 carbon atoms (polymerization temperature 30 °C) have been obtained.

Binuclear neutral nickel(II) complex (**103**) based on the 3,3'-bisalicylaldimine ligand, was synthesized in high yield by Li [63]. Interestingly, this complex, which may be treated as the product of the two **1** molecules coupled at the *ortho* position of the phenoxy group, is capable of polymerizing ethylene without any cocatalyst with an activity of up to $455\text{ kg PE mol Ni}^{-1}\text{ h}^{-1}$ and with M_w up to 487.7 kg mol^{-1} and relatively broad molecular weight distribution ($M_w/M_n = 2.8\text{--}3.8$) were produced. In contrast in the absence of other added activators, complex **1** exhibited no activity for ethylene polymerization. Even when $[\text{Ni}(\text{cod})_2]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ was used as a phosphine acceptor, only a low catalytic activity was observed.

Fig. 2.24 Ethylene homopolymerization by iminopyridine *N*-oxides-based catalysts



Marks [60] reported the synthesis and characterization of novel bimetallic, neutrally charged dinickel 2,7-diimino-1,8-dioxynaphthalene polymerization catalysts. Room-temperature ethylene homopolymerizations were carried out in the presence of the phosphine scavenger/cocatalyst [Ni(cod)₂]. Bimetallic **104**, **105**, and **106** afforded polyethylenes with molecular weights comparable to those produced by the mononuclear analogue **107** and with polydispersities consistent with single-site processes ($M_w \sim 10 \text{ kg mol}^{-1}$, $M_w/M_n = 2.5$). Moreover, the bimetallic catalysts exhibit a 2-fold greater polymerization activity along with increased methyl branching.

In addition to the nature of the copolymer microstructures produced, the mechanism by which the cooperative effects take place was investigated. Low temperature 1 and 2D ¹H NMR spectroscopy of the thermally labile [Ni₂(**C24**)-Bu₂(PPh₃)₂] derivative provides evidence for agostic species in the bimetallic complex. Results evidenced also an agostic interaction of an alkyl group coordinated to one Ni communicating with the second Ni. Such agostic interactions which span both metal centers contribute to Ni ... Ni cooperation. Thus, bimetallic catalysts evidence significant active center-active center cooperative effects in ethylene homopolymerization versus their mononuclear analogues. This cooperativity doubtless arises from the rigidity of the ligands that binds the two Ni centers in close enough proximity (Fig. 2.24).

Recently, Campora devised to replace the anionic aryloxide of salicylaldimine systems with a neutral pyridine *N*-oxide to attain highly active catalysts. Nickel catalysts with 2-iminopyridine *N*-oxides (PymNox) as ligand constitute a promising class of complexes that lead to cationic equivalent of the well-known salicylaldimine system. The electrically neutral *N*-oxide fragment effectively delocalizes the positive charge on the ligand. A series of nickel PymNox complexes with different substitution patterns in the ligand were synthesized [53]. They (**73–79**) are active catalysts for the ethylene polymerization or oligomerization when activated with alumoxanes or diethylaluminum chloride (DEAC). Actually, PymNox nickel catalysts are more active than their neutral salicylaldiminato-based analogues, but the two systems give rise to similar polymers in terms of both molecular weights and branching degree. Electronic effects modulate the activity. An electron-donor group (R³ = OMe) in the remote position 4 of the pyridine ring causes a modest decrease of the catalytic activity and increase of the polyethylene molecular weight, a strong electron-withdrawing group (NO₂) in the same position shifts the catalyst selectivity from ethylene polymerization to oligomerization. More importantly, the introduction of a phenyl substituent in

ortho-position causes a significant increase of the catalytic activity and the polymer molecular weight. Thus, performances of PymNox catalytic systems are strongly reminiscent of those of nickel salicylaldiminates.

The η^3 -benzyl (2-(alkylideneamino)benzoato)nickel complexes in the presence of $B(C_6F_5)_3$ give the zwitterionic η^3 -benzyl complexes active in the polymerization of ethylene (Fig. 2.25). NMR studies with a methallyl complex **108** [61] showed no consumption of ethylene. However, after the mixture stood overnight, the appearance of polymer particles along with the disappearance of the ethylene signal was observed, but signals of the end vinyl group were not detected, which implies that even the molecular weight of the soluble part of the obtained poly(ethylene) was fairly high. In contrast the η^3 -benzyl analogue **109**, which displays faster initiation rates, gave high activity (3,200 kg PE mol Ni^{-1} h $^{-1}$) when the polymerization was initiated at 50 °C, while the activity of the zwitterionic species of **110** is 4,100 kg PE mol Ni^{-1} h $^{-1}$ under the same conditions. The obtained polyethylenes are branched in the range of 35–50 branches/1,000 carbons. The branch number decreases slightly with increase of the pressure. Molecular weights of polyethylene are rather low ($M_w \sim 10$ kg mol $^{-1}$) while the molecular weight distribution is narrow ($M_w/M_n = 2.0$ –2.7), indicating that a single active species is present in the polymerization solution. Even though molecular weights are rather low this result is interesting when considering that the corresponding (2-(diphenylphosphino)benzoato)- and (2-(diphenylamino)benzoato)nickel complexes give mainly butene by a rapid chain transfer reaction.

The chain transfer process is usually reduced by an increase of steric bulkiness on the axial sites, but no increase of the steric bulkiness on the axial sites is observed when the solid structure of the (2-(cyclohexylideneamino)benzoato)nickel complex is compared with that of the (2-(diphenylamino)benzoato)nickel complex. Thus, reduction of the chain transfer process in (2-(alkylideneamino)benzoato)nickel complexes might be explained by a change of electronic effect.

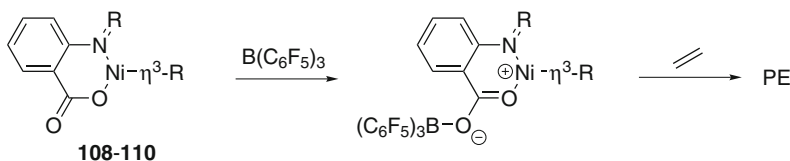
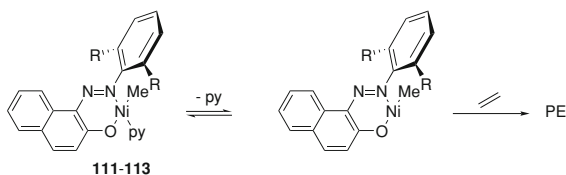


Fig. 2.25 Ethylene homopolymerization by η^3 -R (2-(alkylideneamino)benzoato)nickel catalysts

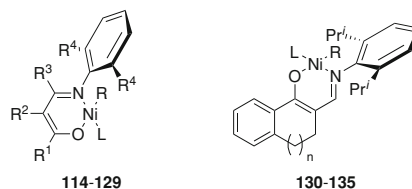
Fig. 2.26 Ethylene homopolymerization by nickel diazene-naphtholato-based catalysts



The search for new ligand structures with other donor functions, empirical to a large extent, though developments had provided some guidelines for catalyst design lead to the synthesis of another class of neutral nickel(II) complexes with chelating diazene ligands [62] as ethylene polymerization catalysts (Fig. 2.26). Well-defined complexes are available as precursors to activator-free catalysts. All complexes **111–113** are moderately active for ethylene oligo- or polymerization, depending on the steric bulk of the substituent on the aryl group. The catalyst bearing the bulky substituted aryl group ($R = ^i\text{Pr}$) (**113**) bound to the diazene function give polymeric materials while a reduction in steric bulk results in a marked decrease in product molecular weight (oligomers). This dependence of the catalytic behavior on the ligand substitution pattern clearly demonstrates coordination of the diazene moiety to the metal center throughout the catalytic reaction. Polymerization requires somewhat elevated temperatures (70–80 °C). The temperature stability is increased by bulky substituents (**113** > **112** > **111**), the catalyst with the less sterically demanding $R = \text{H}$ (**111**) decomposing to a significant extent already at temperatures above 50 °C. The polyethylenes obtained by the complex with the bulky substituted diazene ligand (**113**) has typically $M_w > 50 \text{ kg mol}^{-1}$ and $M_w/M_n = 1.8\text{--}2.3$, indicative of a well-behaved single site catalyst.

Brookhart [64] to further enhance the activity of neutral Ni(II) catalysts synthesized new neutral (N–O) chelated Ni(II) complexes, derived from anilino-substituted enone ligands bearing strongly electron withdrawing $-\text{CF}_3$ and $-\text{C}(\text{O})\text{CF}_3$ [51] in the ligand backbone, and utilized in ethylene polymerization in the presence of an activator as $[\text{Ni}(\text{cod})_2]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ (Fig. 2.27). Polymerizations were generally carried out at ethylene pressures between 7.09 and 28.37 bar and temperatures from 25 to 80 °C. Without the addition of an activator to sequester PPh_3 , that drives the equilibrium toward the $\text{Ni}(\text{ethylene})(\text{alkyl})$ complex, low productivities were observed for complexes **117**, **118** and no polymer was obtained for **119**, **120** even at 14.18 bar of ethylene. This implies, that even at high ethylene pressures the equilibrium lies in favor of the PPh_3 complexes. The productivity under standard conditions (13.78 bar, 60 °C, $[\text{Ni}(\text{cod})_2]$ activator) follows the order **117** > **118** > **119** ~ **120**. The spread in productivities was modest but significant ($14,168 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$ for **117** to $840 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$ for **120**). Moderately branched polyethylenes, generally in the range of 35–55 branches per 1,000 carbons, were produced, consistent with expectations based on the presence of *ortho*-disubstituted aryl groups on nitrogen. It is worth noting that **117**, the most productive and with long lifetime catalyst, is the only one which bears no methyl substituent R^3 to nitrogen.

Fig. 2.27 Catalysts with β -ketoimine frameworks



Neutral β -ketoiminato nickel complexes **121–125**, bearing a bulky substituent at the R^1 position of the ligand, were designed by Li [63–65] et al. This design was based on Grubbs's results that introduction of a bulky substituent at the ortho position of the phenoxy group not only blocks the axial faces of the nickel center and retards the rate of chain termination but also enhances the catalytic activity by accelerating triphenylphosphine dissociation and decreases the rate of catalyst deactivation. Neutral nickel complexes **121–125** were investigated as the catalysts for ethylene polymerization in toluene. The ligand structure significantly affects catalytic activity and polymer microstructure along with properties. Catalyst **121** shows an activity of $13.86 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ using $\text{B}(\text{C}_6\text{F}_5)_3$ as phosphine scavenger ($T = 60^\circ\text{C}$, $pE = 25.33 \text{ bar}$, and B/Ni molar ratio = 1). It is noteworthy that catalyst **122** shows a much higher activity of up to $135.6 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ under the same conditions, which is about 10 times more than the unsubstituted catalyst **121**. Under the same conditions, a comparable catalytic activity of $106 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ was observed for catalyst **123**. These results confirmed that an aryl group in the R^1 position greatly enhances the catalytic activity for ethylene polymerization of the β -ketoiminato neutral nickel catalyst, just like salicylaldiminato neutral nickel catalysts. Probably also with these systems the aryl in the R^1 position plays a key role in protecting the active nickel species from the formation of bis-ligated analogues, proven in salicylaldiminato nickel catalysis to be inactive toward ethylene polymerization. **124** is the catalyst with intrinsically low activity toward ethylene polymerization $5.54 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ while catalyst **125** showed a higher activity of $21.38 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ relative to catalyst **124**, but the activity is still much lower than that of **122**.

The variation of the R^2 group also had a remarkable influence on the branch content and microstructure of the polymer produced, allowing access to the polyethylene whose structure varies from a relatively linear semicrystalline material (with catalyst **122**) to a highly branched (with catalyst **125**) and completely amorphous material.

Moreover, Li [68] succeeded in the synthesis of easily accessible complexes, which are highly active catalysts (**130–135**) for ethylene polymerization without an activator. Under the optimized conditions ($pE = 50.66 \text{ bar}$, $T = 63^\circ\text{C}$) an activity of $70.69 \text{ kg of PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ and M_w of 46.5 kg mol^{-1} were observed using **132** as a catalyst. Particularly, it is of great interest that a bulky substituent proximate to the oxygen atom of the β -ketiminato complex is no longer a prerequisite to attain high catalytic efficiency, which is much different from the case for salicylaldiminato neutral nickel catalysts. Moreover, the degree of conjugation between the phenylene ring and the corresponding nickel chelate of the complex can be tuned via changes in the ligand structure, which remarkably influences the molecular weights and the microstructures of the resulting polyethylenes. The less conjugated complexes **131**, **132** and **134**, **135** produced polyethylenes with much higher molecular weights and lower branching numbers relative to those from the rigid, highly conjugated complexes **130** and **133**.

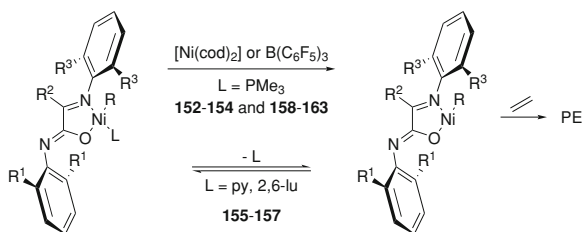
DFT methods gave a rationale of the main difference between these and the salicylaldiminato complexes, that is the high catalytic efficiency of complexes without a bulky substituent at the close position of the coordinating oxygen atom originates from the lower activation energies of these complexes relative to the typical salicylaldiminato complexes.

The synthesis of a new organometallic nickel complexes supported by the 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate ligand **129** [67] allowed for the investigation of remote activation through an exocyclic CN functionality. The binding of $B(C_6F_5)_3$ to the carbonitrile nitrogen results in a redistribution of electron density within the electronically delocalized ligand framework and initiates the homopolymerization of ethylene. The resulting polymers are described by monomodal molecular weight distributions. This complex, activated via an exocyclic CN functionality, opens new ways to design of appropriate ligands for zwitterionic ethylene polymerization initiators.

Aryl nickel phosphine complexes containing pyridine carboxylate ligands represent the first example of single component catalysts for oligo- or polymerization of ethylene [71, 72]. Electronic effects on nickel-catalyzed oligomerizations/polymerizations were delineated through the use of a series of substituted pyridine carboxylate complexes (**138–145**). Lower basicity of the substituted pyca ligand facilitated migratory insertion and therefore chain growth. At 80 °C and 40 bar, the electron-rich methoxy substituted catalyst (**146**) gave mostly linear olefins (56%) with only 10–20 % of the product consisting of higher molecular weight polyethylene. The electron deficient nitro-substituted catalyst (**147**) produced between 80 and 100% of high molecular weight PE under similar conditions. In addition, the nitro-substituted catalyst gave the highest activities of all these complexes.

The α -iminocarboxamide ligands were selected by Bazan who first thought that metal activation by formation of carbonyl adducts could form the basis of a new strategy for designing novel nickel olefin polymerization catalysts (Fig. 2.28) [73]. It was disclosed that the activation of **152** with $[Ni(cod)_2]$ results in an active olefin polymerization catalyst which is capable of catalyzing the quasi-living homopolymerization of ethylene. Polymerizations were conducted at 7.09 bar, 20 °C and for 20 min. No polyethylene was formed when **152** was used alone. There is a sharp increase in reactivity when the $[Ni(cod)_2]/\mathbf{152}$ ratio increases from 1 to ca. 2.5, followed by a slower increase in activity as this ratio approaches. NMR spectroscopy showed that the polyethylene has a relatively low branching content

Fig. 2.28 Ethylene homopolymerization by α -iminocarboxamide nickel catalysts



(10–20 Me branches per 1,000 C). The molecular weight distributions are monomodal but not as narrow as those of a truly living system; the authors proposed this results from an initiation step considerably slower than the propagation and from the precipitation of the polymer.

The α -iminocarboxamide species **155** and **156**, [96] that take advantage of pyridine ligand instead of PMe_3 as **152**, are single-component initiators for the polymerization of ethylene. There is no need to use $[\text{Ni}(\text{cod})_2]$ for activation, as is the case for the PMe_3 analogues. However, the thermal activation required for dissociation of py or 2,6-lu probably reduces the control over the polymer structure; that is, it was not possible to find polymerization conditions with quasi-living characteristics. The polymerizations with **156** can be accomplished under milder reaction conditions, relative to **155**. Best results in activity ($304 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$) and molecular weight (M_w 143 kg mol^{-1} , $M_w/M_n = 2.2$) were obtained in the presence of **156** at $pE = 6.89 \text{ bar}$ and $T = 40^\circ\text{C}$.

More recently, neutral nickel complexes containing α -iminocarboxamide, $\eta^1\text{-CH}_2\text{Ph}$, and PMe_3 ligands were synthesized by Bazan [75] and used in the homopolymerization of ethylene. In particular, the effect of steric and electronic variations at the site adjacent to the imine functionality was studied. Ethylene homopolymerization reactions were performed using complexes **154**, **158–163** and $[\text{Ni}(\text{cod})_2]$ as activator. Polymerizations were carried in toluene at an ethylene pressure of 7.09 bar at 20°C . The polymerization activity increases as the bulk on the ligand framework increases i.e. **154** < **158** ~ **161** < **159** < **160**. The isopropyl derivative **160** exhibits an activity > 2-fold as compared to the parent methyl species **152**. The M_n of the polymer products also increases proportionally with the increase in activity. Compound **160** exhibits the lowest molecular weight distribution ($M_w/M_n \sim 1.2$) when compared to the other alkyl variants.

In the case of **161**, the activity and molecular weight observed are higher than those obtained with the parent species **152**. The molecular weight and activity are higher for compound **162** and lower for **163** relative to **161**. This trend suggests that as electron density is removed from the metal center, the catalytic species becomes more active in ethylene polymerization reactions (i.e., reactivity: **162** > **161** > **163**). Polyethylene made with compounds **161–163** exhibits the narrowest polydispersities, between 1.1 and 1.2 in all cases.

A new family of ligands based iminohydroxamate backbone and their transition metal halide complexes were proposed by Bildstein [76] as new precatalysts for MAO activated olefin polymerizations. Ethylene polymerizations were performed in toluene, at a temperature of 70°C at pE of 40 bar . In terms of activity, only compound **164** truly stands out as a precatalyst with a high activity of $302.8 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ but in short polymerization time. Indeed, the stability of the $[\text{N,O}]\text{NiBr}_2$ complexes **164–167** in their MAO-activated form has not yet been optimized, indicating fast deactivation pathways. PE samples obtained from nickel complexes **164–167** were of the HDPE type with no detectable branches and molar masses (M_v) of 1.0 to 250 kg mol^{-1} .

Brookhart [77, 78] designed a ligand which incorporated the key elements of the six-membered chelate salicylaldimine ligand but which would lead instead to a

five-membered chelate. He chose for this purpose the 2-anilintropone moiety because it contained the desired anionic N,O chelate, a hindered N-aryl group, and complete conjugation between the N and O. The corresponding highly neutral nickel catalyst is active in ethylene polymerization and it does not require an activator (Fig. 2.29).

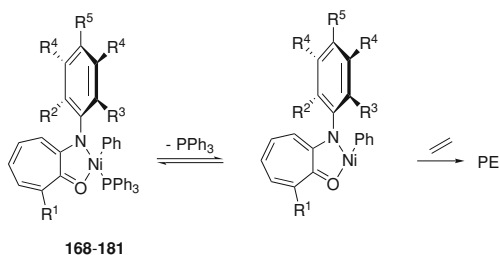
Under optimized conditions, catalyst **169** can produce PE, without the addition of a cocatalyst, with a TOF of 8.8×10^3 kg of PE mol Ni⁻¹ h⁻¹ in a 10 min run. Additionally, **169** produced PE with a substantially higher M_n when compared with the salicylaldimino type bearing the anthryl substituent in the *ortho* position (89.6 vs. 54 kg mol⁻¹). Nevertheless **169** shows a short lifetime when compared to 2-salicylaldimino type bearing the anthryl substituent. Ethylene pressure has also been shown to have dramatic effects on the resultant PE. Increasing the pressure from 1.01 to 40.53 bar at 80 °C causes a decrease in the branching number from 113 to 41 branches per 1,000 C.

Moreover, a series of anilintropone ligands and corresponding nickel complexes was synthesized in an effort to determine the effects of varying the *ortho*-aryl substituents on ethylene polymerization. Catalysts incorporating alkyl substituents at the 2- and 6-positions of the N-aryl ring generated high-molecular-weight polyethylenes with monomodal molecular weight distributions of ca. 2 (or less at low temperatures). Total turnover numbers of ca. 60,000 were observed in 10 min at 80 °C, but catalyst lifetimes are short at this temperature. Branching increases with increasing temperature and decreasing pressure, consistent with earlier observations using aryl-substituted diimine catalysts.

Replacement of the standard 2,6-diisopropyl substituents on the aryl group with 2,6-dimethyl (**168**), 2,6-dichloro (**173**), 2,6-dibromo (**174**), and 2-methyl-6-trifluoromethyl (**178**) substituents had little effect on productivity. A slight increase in TON was observed for the 2,6-diphenyl-substituted catalyst (**172**). Significant reduction in TON was observed for the 2-methyl-6-tert-butyl- (**171**), 2-methyl- (**177**), 2-tert-butyl- (**170**), and 2,3,4,5,6-pentafluoro-substituted (**175**) catalysts. Molecular weights generally increase with increasing steric bulk of the *ortho* substituents.

Substitution of the 2-(2,6-diisopropylanilino)tropone ligand with either phenyl (**180**) or naphthyl (**181**) groups resulted in a small increase in productivities and lifetimes at 80 °C and 14.18 bar. However, at 40 °C these catalysts exhibited much longer lifetimes ($t_{1/2} > 1$ h) and higher total turnover numbers

Fig. 2.29 Anilintropone-based catalysts for ethylene polymerization



could be achieved relative to 80 °C polymerizations. Molecular weights of the polyethylenes increased with pressure, which suggests that chain transfer at least in part occurs through classical β -H elimination rather than chain transfer to monomer. The catalyst decay product is the Ni(II) bis-ligand complex, whose formation must be initiated by reductive elimination of the ligand from a Ni(II) species.

The anilinoperinaphthenone nickel complexes **183**, **184** [80] are active ethylene polymerization catalysts and **184** is significantly more reactive than **183** with turnover numbers of 47,000 and 8,000, respectively, under identical reaction conditions (14 atm ethylene, 80 °C). The number average molecular weight under these conditions is 99,000 with a $M_w/M_n = 1.9$ and significantly increases with ethylene pressure (e.g., $M_n = 37 \text{ kg mol}^{-1}$ at 3.04 bar, 80 °C; 54 kg mol^{-1} at 7.09 bar, 80 °C) suggesting that chain transfer to monomer is not the major chain transfer mechanism. As temperature increased from 40 to 100 °C, with pressure held constant at 14 atm ethylene, the number average molecular weight of the polymer decreased and the branching number increased from 17 to 66 branches per 1,000 carbon atoms. The catalyst half-life is ca. 20–30 min. In conclusion, these catalysts have an activity that is similar to the previously reported anilintropone based neutral nickel(II) ethylene polymerization catalysts. The similarity in overall activity suggests that the lack of delocalization of electron density onto the oxygen atom has little effect on catalyst performance.

A novel nickel complex ligated with 2-(2,6-diisopropylanilino)-1,4-naphthoquinone (**185**) was synthesized by Shiono [81]. This complex polymerized ethylene at 40 °C to give linear polyethylene in low yield. On the other hand, **185** when activated with 4 eq of $\text{B}(\text{C}_6\text{F}_5)_3$ was highly active for ethylene polymerization and gave a polymer possessing short methyl, ethyl, and propyl chain branches formed by a chain walking mechanism, as well as long chain branches, the content of long chain branches was almost the same as that of all short chain branches. Thus, the macromonomer formed via β -H elimination were effectively copolymerized with ethylene to give the long chain branches.

Later on, a series of nickel complexes (**186–188**) bearing anilino-naphthoquinone derivatives possessing different substituents were synthesized [82]. Decreasing the bulkiness of 2,6-substitution on anilines lowered the polymerization activity as well as the molecular weight of the polymer produced. In contrast, the methyl substitution at 4-position of aniline increased the polymerization activity and the molecular weight of the products. This indicates that polymerization activity and molecular weight depended on the electronic state of the metal center as well as the bulkiness of 2,6-substitution on anilines. The molecular weight of the obtained polymer increased lowering the temperature, indicating that the β -H elimination is more suppressed than propagation at low temperature. This trend is more notable with the complex with the less bulky substituent on aniline 2,6-position. These complexes produce short chain branches such as methyl, ethyl, and propyl as well as long chain branches. The branching amounts decreased in the more bulky systems, indicating that chain migration was suppressed by introducing bulky substituent at 2,6-position of aniline.

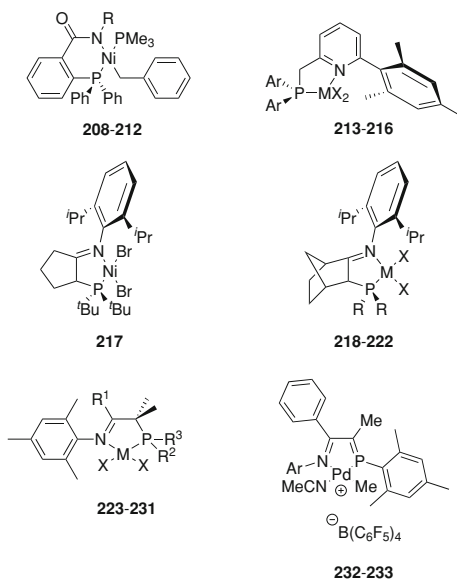
New, neutral binuclear nickel(II) complexes with bridging ligands comprising 2,5-disubstituted amino-*p*-benzoquinones (**189–193**) have been synthesized and tested in the ethylene polymerization without any cocatalysts [83]. The complexes are catalytically active in ethylene polymerization. Particularly, complex **189**, comprising a bulky substituted aryl group bound to the anilino function, has activity comparable to that of the Grubbs catalyst **3** under the same conditions. A reduction in steric bulk resulted in a marked activity decrease while the optimum polymerization temperature seems to be 80 °C. Polyethylene obtained employing complexes **189–191** revealed molecular weights of $M_w = 4.31, 535,$ and 60.3 kg mol^{-1} , respectively. The molecular weight distribution is quite wide (3.21–48.24) and quite different from those of well-behaved single-site catalysts. Methyl branches predominate with ca. 10 methyl branches per 1,000 carbon atoms but additional higher branches, such as butyl, are also present.

In the course of their studies on metal complexes of amino acids and their derivatives Beck et al. [84] reported the synthesis of aryl complexes of nickel and palladium with the “classical” α -amino carboxylates as N–O-chelate ligands which may have catalytic activity. The complex **194** is, in the presence of AlEt_3 , a highly active catalyst for the polymerization of ethylene (up to $1,800 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$). The polymerization started with a high activity peak. Polymers with high molecular weights (up to 900 kg mol^{-1}) were obtained. In comparison with the related nickel complexes by Cavell (**147**), Keim and Grubbs (**1–10**) and their co-workers complex **194** affords polymers with remarkably high molecular weights and with much less branching.

The quest for identifying novel Ni(II) and Pd(II) catalysts bearing bulky bidentate ligands which would expand the scope of utility of such catalysts encouraged considerable efforts. The interest to have catalysts with higher thermal stability than bisimine Ni(II) and Pd(II) catalysts which decompose rapidly at about 70 and 50 °C, respectively prompted towards the synthesis of late transition metal complexes with various phosphine nitrogen (P–N) ligands (Fig. 2.30).

Ni(II) and Pd(II) complexes (**217–219**) with phosphine imine hybrid ligands were successfully synthesized by Guan [34]. The Ni(P–N) complexes assume a tetrahedral coordination geometry, while the Pd(P–N) complexes are all square planar. The Ni complexes, upon activation with MAO, were active for ethylene polymerization and significantly more stable than the corresponding Ni-diimine complexes, whereas the activities of these catalysts are lower than those of the Ni-diimine complexes. Complex **219** was much more active than **217–218** and this is presumably due to differences in the electronic structure. The phosphine in **217–218** is much more electron rich than the phosphine in **219** because the ^{*t*}Bu group has stronger electron donating ability than the phenyl group. On the other hand, the lower molecular weight of polyethylene obtained with complex **219** is attributed to the decreased steric bulkiness of the diphenylphosphine as compared to the di-*tert*-butylphosphine in **217–218**. In complex **217** the chain transfer process should be reduced by the orientation of both the ^{*t*}Bu groups from phosphine and the isopropyl groups of aniline towards the axial positions. However, the asymmetry of the steric bulkiness for **217**, the top axial face being much more

Fig. 2.30 Catalysts with N–P mixed chelating ligands



open than the bottom one, makes the metal center susceptible to chain transfer. This is presumably the cause for the formation of polyethylenes with relatively low molecular weight in the ethylene polymerization catalyzed by the Ni(P–N) complexes. Another remarkable feature of ethylene polymerization by the Ni(P–N) complexes is that the polyethylenes formed contain much more branches (50–60 total branches per 1,000 C) than the polyethylenes by diimine complexes under similar conditions. Significant amounts of relatively long branches (such as amyl and hexyl) are formed. The presence of ethyl in isobutyl groups reveals the existence of short branch on-branches. Thus, chain walking is more competitive with complexes **217–219** than in the Ni-diimine system. In contrast, all the Pd(P–N) complexes **220–222** upon activation with MAO were inactive to polymerize ethylene probably due to their electronic structure. The major fraction of the polyethylene obtained by Guan had low M_w in the range of a few thousands, but the minor fraction consisted of very high molecular weight polymer (M_w up to 10^3 kg mol^{-1}). Brookhart hypothesized that at high temperatures used by Guan the catalyst backbone is easily enolizable which is partially chemically modified, and this modification is responsible for the low molecular weight fraction in the polymer.

Thus, bulky nonenolizable phosphineimine Ni(II) (**223–227**) and Pd(II) (**228–231**) complexes from bidentate ligands were prepared by Brookhart [35] with the hope of obtaining thermally stable polymerization catalysts which would produce high molecular weight, branched polyethylene. They did show improved temperature stability with respect to the corresponding diimine complexes.

At 80 °C the palladium catalysts oligomerize ethylene giving branched oligomers with M_n up to 0.66 kg mol^{-1} . Reaction of **229** with $\text{NaB}(\text{C}_6\text{F}_5)_4$ generates

the ion-pair $[\text{Pd}(\text{V2})\text{Me}][\text{B}(\text{C}_6\text{F}_5)_4]$ that is unable to polymerize ethylene. In the iminephosphine palladium complexes the situation is unfavorable for migratory insertion since in the more stable isomer of $[\text{Pd}(\text{V2})\text{Me}]^+$ the Pd–Me bond is expected to be stronger than the Pd–Me bond in diphosphine while the Pd–ethylene interaction is stronger than that in the diimine ligands. Thus, the stability of the methyl ethylene “unit” is greatest in $[\text{Pd}(\text{V2})(\text{h}^2\text{-C}_2\text{H}_4)\text{Me}][\text{B}(\text{C}_6\text{F}_5)_4]$. The migratory insertion barrier of ethylene into the Pd–Me bond was shown to be $24.8(3) \text{ kcal mol}^{-1}$, which is ca. 8 kcal mol^{-1} higher than the corresponding barriers in diimine and diphosphine palladium complexes.

The nickel dimethyl-substituted complex **223** was used to screen the behavior and efficiency of several aluminum alkyl derived activators. The use of ethylaluminum dichloride led to the production of butenes with $\text{TO h}^{-1} > 10^6$ in an exothermic reaction. Activation with DEAC resulted in the production of butenes and only polymer traces. Polymethylaluminoxane (PMAO–IP) afforded both butenes and polymer while the use of MMAO–3A under 27.86 bar of ethylene at room temperature gave exclusively polymer with $M_n = 2.4 \text{ kg mol}^{-1}$ and $1,000 \text{ kg PE mol Ni}^{-1} \text{ h}^{-1}$.

Catalyst **225** would be more reactive than dimethyl-substituted complex **223** and give high molecular weight product. Unexpectedly, only a small amount of polymer with a bimodal molecular weight distribution ($M_p = 37.2; 3.1 \text{ kg mol}^{-1}$) was obtained while diphenyl-substituted precatalyst **224** was found to be more effective producing an elastomeric material with $M_n = 72 \text{ kg mol}^{-1}$ and $M_w = 133 \text{ kg mol}^{-1}$. Increase of steric bulk at phosphorus, as in **227**, gives rise to lower molecular weight material ($M_w = 75$ vs. 140 kg mol^{-1} for diphenyl-substituted precatalyst).

The polymer produced by **224** has almost exclusively methyl branches while that formed by **227** at 60°C contains a great amount of higher branches. In general, polyethylenes obtained using catalysts **223–227** are substantially more branched than polymers obtained by Ni-diimine catalysts under similar conditions.

Finally, nickel imine-phosphine precatalysts containing gemdimethyl substituent α to phosphorus produce substantially higher molecular weight polyethylene compared to the corresponding enolizable complexes.

Pd(II) catalysts incorporating phosphinidine-imine ligands were also synthesized by Brookhart [92]. Complexes **232–233** proved to be ethylene oligomerization catalysts and were studied at 26°C and 400 psi ethylene. They exhibit very low turnover rates, the more hindered catalyst **232** in a 3 h run yielded $23 \text{ kg PE mol Pd}^{-1}$. Higher turnover numbers ($94 \text{ kg PE mol Pd}^{-1}$) were observed with decreased hindrance in **233** along with a drop of oligomer molecular weight from 0.67 to 0.3 kg mol^{-1} . The catalysts are more stable than Pd–diimine complexes at room temperature; they do not significantly deactivate in 15 h. Ethylene insertion barriers were measured for the less hindered mesitylimine system **233** by generating the cationic ethylene complex with $\text{NaB}(\text{C}_6\text{F}_5)_4$ under excess olefin (20 eq). Insertion of ethylene into Pd–alkyl bonds was measured $18.7 \text{ kcal mol}^{-1}$. For comparison, typical migratory insertion barriers in (diimine)palladium(methyl)(ethylene)

complexes are ca. 17 kcal mol⁻¹, that is 2 kcal higher than the insertion into barriers in Pd(diimine)Me(ethylene) complexes.

Ni and Pd complexes **213–216** [91] with P–N ligands linked by a nonenolizable rigid carbon framework were designed. The steric bulk was created by introducing substituents at the 6-position of pyridine and a mesityl or tolyl group on the phosphorus atom. The palladium complexes are inactive in the polymerization of ethylene. In fact, palladium black was obtained in most instances, indicating the instability of these palladium complexes under the reaction conditions. The behaviour of nickel complexes in oligo- or polymerization of ethylene is quite different from that of the palladium species. With a molar ratio of MAO to complex of 150:1, complex **213** catalyzed the polymerization of ethylene to form PE in poor yields with a bimodal molecular weight distribution. Butenes and hexenes were obtained in high conversions when a larger quantity of MAO (Al/Ni = 500) is used. The nickel(II) dibromo complexes were highly active in the presence of MAO. With a lower Al/Ni ratio, the nickel complexes catalyzed the polymerization of ethylene, yielding an orthorhombic form.

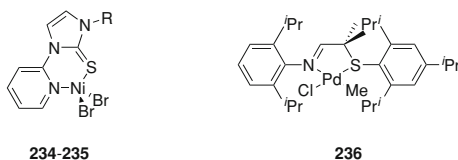
Zwitterionic 2-diphenylphosphanylbenzamido nickel(II) complexes [Ph₂PC₆H₄C(O)NR- κ^2 -N,P]Ni(η^3 -CH₂Ph) (R = C₆H₅, (**208**); R = ^tBu, (**209**); R = H, (**210**); R = Pr, (**211**); R = ⁱPr, (**212**) were prepared by Lee [73] and tested in the ethylene polymerization. Generally, in both N–N and N–O late transition metal complexes, steric factors regulate the balance between the chain propagation and the chain transfers. High molecular-weight polyethylene is obtained by sterically congested complexes. However, there are some examples showing that electronic effects of the ligand also may play an important role in determining polymer molecular weight.

Slight changes in the ligand frame of complexes **208–212** result in big differences on the products [90]. Phenylamido complex **208** is unable to oligomerize ethylene under the pressure of 6.89 bar, at room temperature and gives 1-butene. Additions of ethylene gas to complexes **209–212** give mainly butene with relatively low activities (230–300 kg PE mol Ni⁻¹ h⁻¹). However, isopropylamido complex **212** gives excellent activity at room temperature (2,300 kg PE mol Ni⁻¹ h⁻¹). When the polymerization temperature is raised to 50 °C, the activity increases to 5,200 kg PE mol Ni⁻¹ h⁻¹, which is a quite high value among the activities observed for similar-type zwitterionic nickel complexes. The molecular weight of the polymers is considerably high ($M_w \sim 1,300$ kg mol⁻¹) but rather broad molecular weight distributions ($M_w/M_n \sim 2.8$ – 3.7) were observed, most probably for the difficulty to keep the polymerization under control for the very high activity.

The enormous differences in molar masses could not be easily explained since the two solid structures of **208** and **212** are quite similar. Since a big difference is observed on the angles between the square plane and the benzamide benzene ring it was suggested that, probably, when the angle is steep as observed for **212**, there is a shielding of the other axial site by π -electrons on the benzamide ring.

Only very few reports are in the literature of attempts to substitute one imine with sulphide groups. The results reported below explain such scarcity.

Fig. 2.31 Rare examples of catalysts with N–S ligands



Brookhart prepared the imine-sulfide palladium(II) complex **236** [92] in an effort to increase the molecular weight of the oligomer/polymer produced with a phosphinidine-imine catalysts (see above). It was expected that geminal dimethyl groups on the chelate backbone of **236** should impart a more restricted conformation to the S-aryl group, thus leading to more effective blocking of the axial sites.

In an NMR experiment **236** activated with $\text{NaB}(\text{C}_6\text{F}_5)_4$ completely consumed ethylene, but in a preparative run under 1.01 bar of ethylene afforded small amount of polyethylene with $M_n = 2.8 \text{ kg mol}^{-1}$ in 44 h. Under 27.86 bar of ethylene, only a small amount (54 mg/3 h; 72 mg/15 h) of polyethylene with $M_n = 1.8 \text{ kg mol}^{-1}$ was obtained. Since the high pressure experiment afforded less polyethylene than the 1 atm run, probably under high pressure of ethylene the ligand is displaced from the palladium and thus the catalyst decomposes as confirmed by the precipitation of palladium black (Fig. 2.31).

More recently, the nickel complexes **234–235** [93] bearing bulky N-substituents were synthesized, they possess potentially reactive sites for the ethylene polymerization. However, unfortunately, after activation with MAO, nickel complex **235** with the bulkier N-2,6-diisopropylphenyl substituent catalyzed ethylene to waxes with low activity at atmosphere pressure. By increasing ethylene pressure to 7 bar only small amount of high molecular weight PE was obtained, while the complex **235** bearing N-*i*-butyl substituent gave only waxes under the same condition. The catalyst activity of **235** to high molecular weight PE was lower than those of the pyridylimine nickel complexes and α -diimine nickel catalysts. Probably steric bulky at only one arm side (imidazole N-substituent) resulted in chain propagation slower than chain transfer in contrast to the α -diimine nickel catalysts with two bulky arm sides. Additional possible reasons for the low activity to high molecular weight PE are in non square planar arrangement of the pyridine and the imidazole rings which lead to deviation of the steric bulk introduced from the axial sites.

2.4.3 Copolymerization of Ethylene with Monomers with Functional Groups

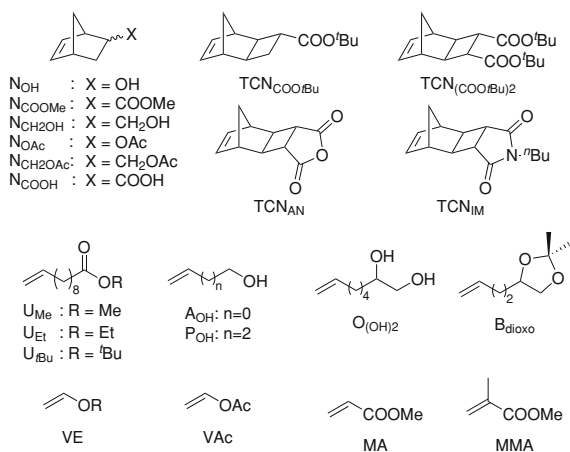
The selective introduction of functional groups into aliphatic polyolefin backbones represents a pivotal and overdue issue in polyolefin technology. Since they can

significantly control surface material properties, such as adhesion, wettability, dyeability, and printability as well as compatibility. Despite the tremendous advances in organometallic-catalyzed olefin polymerization, industrial incorporation of polar monomers in polyolefins still exploits radical polymerization. Radical polymerization provides branched polymers and highly-functionalized copolymers having physical properties not comparable to those of linear polyolefins.

Catalysts based on Ni and Pd, with respect to those based on early transition metals employed in industry, are intrinsically less sensitive to functional groups, as a result of their less oxophilic nature. Certainly they are well far away to be unfailing and any functionalized monomer represents a specific issue in terms of productivity, degree of functionalization, molar mass, etc. Specifically, for any monomer the possible interactions between the main-group functionality and the metal center before and after insertion should be considered. The recent advances in olefin-polymerization catalysts based on late transition metals allow for incorporating most of polar functionalities. For example, N–N Pd-based systems tolerate acrylates, vinyl ketones, and silyl vinyl ethers, they fail with others such as vinyl acetate, vinyl chloride, and acrylonitrile; in any case they afford hyper-branched copolymers with functionalities located mainly at the end of ramifications. Differently, Ni-based systems were reported to afford linear copolymers of ethylene and MA but with extremely low productivity.

Some promising results were reported by catalysts with nitrogen-based mixed chelating ligands. The functionalized monomers so far copolymerized with ethylene by Ni and Pd catalysts bearing nitrogen-based mixed ligands are listed in Fig. 2.32. The monomers are namely functionalized norbornenes, functionalized α -olefins, and polar vinyl monomers, whose C–C double bond is directly substituted by polar functional groups. The norbornene derivatives have the functional group distant from the double bond and are more easily incorporated than functionalized α -olefins. Incorporation of 2–4 mol% of functionalized norbornenes would be enough for depressing the polyethylene melting point and serves as a

Fig. 2.32 Functionalized norbornenes, functionalized α -olefins, and polar vinyl monomers copolymerized with ethylene by N–Z-containing catalysts



starting point for testing comonomers that can be incorporated and to what extent. Their features will be discussed in detail in the text along with the behavior with catalysts involved.

Copolymerization reactions of ethylene with functionalized monomers catalyzed by nickel (salicylaldiminato)-based catalysts are summarized in Fig. 2.33.

Complexes **5** and **8** were early reported as single-component catalysts for the copolymerization of ethylene with functionalized norbornene derivatives N_{OH} and N_{COOMe} affording $\text{P(E-co-N}_{\text{OH}})$ with the N_{OH} incorporation of 22 wt%, $M_w = 17.2 \text{ kg mol}^{-1}$, and $M_w/M_n = 1.6$ and $\text{P(E-co-N}_{\text{COOMe}})$ with the N_{COOMe} incorporation of 12 wt% and $M_w = 73.8 \text{ kg mol}^{-1}$, respectively [2]. In the pioneer report the authors pointed out polar group tolerance and effective incorporation of functionalized monomers while neither activities nor difference in catalytic behaviour were discussed. A more exhaustive investigation revealed that acetonitrile-containing catalyst **8** demonstrated a higher activity than the phosphine-containing analogous **5** due to the easier activation, in analogy with ethylene homopolymerization [97].

Copolymerization of ethylene with functionalized norbornene derivatives was extended to monomers $\text{N}_{\text{CH}_2\text{OH}}$ and N_{OAc} . As expected monomers N_{COOMe} and N_{OAc} bearing ester groups resulted less poisoning than the protic $\text{N}_{\text{CH}_2\text{OH}}$ as showed by productivities and molar masses. In addition, the higher the steric demand of substituent onto the comonomer the lower the incorporation (in the

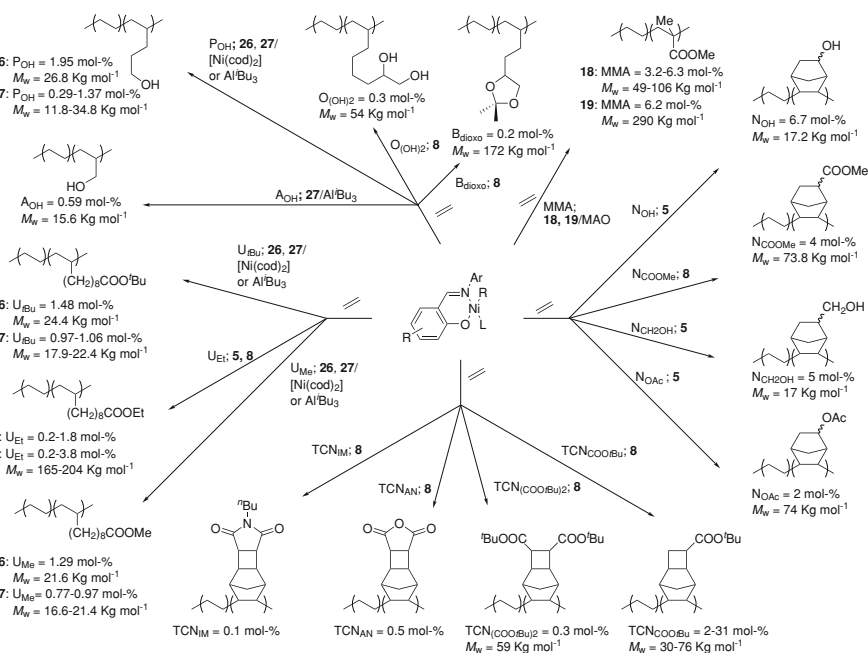


Fig. 2.33 Functionalized ethylene copolymers obtained by salicylaldiminato complexes

order $N_{\text{COOMe}} < N_{\text{OAc}} < N_{\text{CH}_2\text{OH}}$). Since starting monomers were used as isomer mixture, this trend is ascribable to *endo* isomers, which after insertion are prone to give chelated intermediates, that block the vacant coordination site of catalyst. In this regard, tricyclononene-based functionalized monomers ($\text{TCN}_{\text{COO}t\text{Bu}}$, $\text{TCN}_{(\text{COO}t\text{Bu})_2}$, TCN_{AN} , TCN_{IM}) were expected to be more readily incorporated than bicyclic analogues for the higher distance of polar functionality from olefin double bond. Indeed, catalyst **8** showed a 3.5-fold higher TON in copolymerization of ethylene with monomer $\text{TCN}_{\text{COO}t\text{Bu}}$ than with the monomer N_{COOMe} in similar experiment. Interestingly, incorporation of monomer $\text{TCN}_{\text{COO}t\text{Bu}}$ could be tuned from 2 to 31 mol% through $\text{TCN}_{\text{COO}t\text{Bu}}/\text{E}$ feed ratio, though productivity dropped down with decreasing E concentration. Other interesting aspects of these uncommon tricyclic monomers were discussed on the basis of their chemical diversity.

Functionalized α -olefins such as alkyl undecylenoate esters U_{Me} , U_{Et} , and $\text{U}_{t\text{Bu}}$ were successfully copolymerized with ethylene by catalysts **5**, **8** [39, 97], **26** [45], and **27** [46]. Activities of these reactions are approximately one order of magnitude lower than in E homopolymerization in non-coordinating medium (toluene, benzene) but resemble those obtained in more coordinating solvents (ether, esters) [2]. Again, acetonitrile-containing catalyst **8** exhibited higher activities than phosphine-containing **5**, **26**, and **27**. Though to some extent less active, catalyst **26** bearing the cyclohexyl substituent at the ortho position of the phenoxy group showed a slightly higher incorporation of functionalized monomers than anthracenyl-substituted analogues **5** and **8**.

A series of copolymers containing monomer U_{Et} in different concentration was prepared by catalysts **5** and **8**. The resulting materials moved from HDPE to LLDPE domain ($\text{U}_{\text{Et}} = 10$ mol%). T_m values reflected the composition and decrease with comonomer incorporation as expected.

Interestingly, the ester-functionalized olefins significantly reduce the formation of short alkyl branches (Me, Et, Pr, and Bu) compared to those in ethylene homopolymerization and copolymerization with α -olefins such as 1-octene. This suggests that coordination of polar functionalities competes with β -H agostic interaction, preventing elimination side reactions.

More problematical was the copolymerization of ethylene with free alcoholic monomers A_{OH} and P_{OH} that can hydrolyze Ni-polymeryl bond, protonate the N–O ligand, and favor the displacement. The approach of protecting the alcoholic monomer with Al^iBu_3 was exploited for the copolymerization of ethylene with monomers A_{OH} and P_{OH} by catalyst **26–27** that furnished $\text{P}(\text{E-co-A}_{\text{OH}})$ in good yield ($M_w = 26.8 \text{ kg mol}^{-1}$, $M_w/M_n = 2.29$, $\text{A}_{\text{OH}} = 1.95$ mol%). On the other hand, catalyst **8** gave a poor yield and a polymer with low M_w without protecting the diol-containing monomer $\text{O}_{(\text{OH})_2}$ whereas furnished activity and M_w values as good as in the reactions involving the ester-based monomer U_{Et} when the similar dioxolane B_{dioxo} was copolymerized.

A different and challenging task is represented by (co)polymerization of electron-deficient vinyl monomers such as acrylates. Modification of the energy of frontier orbitals as well as proximity of polar functionality to olefinic double bond

had made the coordination polymerization of these monomers elusive for a long time. A prerequisite for the incorporation of polar vinyl monomers is that π -coordination of the olefin double bond is competitive with the heteroatom σ -coordination.

Indeed, attempts to copolymerize ethylene with MA, VAC, and VE by catalyst **5** and **8** failed. An in-depth NMR investigation of organometallic species and decomposition product originating from interaction of more sophisticated salicylaldimino-based catalysts and MA revealed that after the first insertion of MA no further E or MA insertion occurs; VA behaves similarly [97].

MMA is definitely one of the most challenging functionalized monomer to be copolymerized with ethylene because besides the aforementioned features of electron-deficient vinyl monomers it possesses a *gem*-disubstituted olefinic carbon.

Preliminary trials, which exploited bischelated complexes activated by MAO, produced high MMA content materials ($61 < \text{MMA} < 81 \text{ mol}\%$) but molar masses, polydispersities, and microstructure of MMA sequences suggest the cooperation of radical and coordinative mechanism [99]. Conversely, copolymerization by complexes **18** and **19**, which contain nitro groups onto phenoxy ring, activated by MAO (Al/Ni = 15/1) in the presence of ethylene atmosphere ($p\text{E} = 50 \text{ atm}$) afforded high molar mass P(E-*co*-MMA) with an incorporation of MMA of 3–7 mol% and T_m values of about 130 °C, indicating the high linearity of the products.

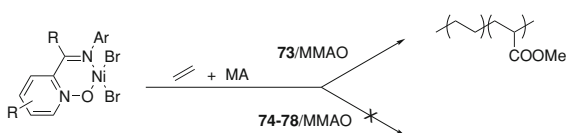
Iminopyridine *N*-oxide-based complexes **73–78** activated by MMAO were investigated as catalysts for the copolymerization of ethylene with MA (Fig. 2.34). Except for **73**, which effectively furnished P(E-*co*-MA) in low yield and molar mass ($M_n = 1.9 \text{ kg mol}^{-1}$) with low incorporation of comonomer (0.7 mol%), the addition of MA resulted in a complete deactivation of the catalysts.

Copolymerization of ethylene with polar monomers by bimetallic catalysts, which are generally and intrinsically more active than their monometallic analogous, can profit from cooperative effects arising from the close proximity of two metal centers [100].

Indeed, a clear and positive effect of dinuclearity was demonstrated by catalysts **100–102**/B(C₆F₅)₃ in copolymerization of ethylene with functionalized norbornene derivatives N_{COOMe} and N_{CH₂OAc} (Fig. 2.35) [58].

A series of E-*co*-N_{CH₂OAc} copolymerizations by the three catalysts revealed a 2-fold higher activity as well as higher incorporation of functionalized monomer than mononuclear **56** analogous in the same conditions. Complex **102**, which possesses the terphenyl *o*-C₆H₄(C₆H₄)₂ group as bridging unit between the two salicylaldimine cores, exhibited the highest incorporation (14–42 mol%). Effect of dinuclearity on activity, incorporation, and best performance of catalyst **102** was

Fig. 2.34 Linear ethylene copolymers with MA by iminopyridine *N*-oxides-based catalysts



confirmed also for monomer N_{COOMe} . Experimental evidence and theoretical calculations suggested the effective action of a cooperative effect between the two metal centers.

Binuclear naphthyloxydiiminato nickel catalysts **104** and **106** activated by $[Ni(cod)_2]$ efficiently copolymerize a variety of functionalized monomers ranging from norbornene derivatives to acrylates (Fig. 2.36) [100].

The effective occurrence of eventual cooperative effects in copolymerization of ethylene with monomers N_{OH} , N_{COOMe} , N_{CH_2OH} was demonstrated by comparing bimetallic systems with monometallic **57** and **58**. Activities as well as incorporation of functionalized monomers of bimetallic catalysts 3–4-fold higher than monometallic analogue in identical conditions confirmed the higher selectivity for the enchainment of polar components. Interestingly, molar masses of copolymers are similar to those of copolymers of ethylene with norbornene. Attempts to enchain N_{COOH} failed because the high acidity of the comonomer leads to catalyst deactivation by protonation of hydroxyl ligands with consequent ligand displacement as confirmed by 1H NMR experiments.

In addition to norbornene derivatives, catalysts **104** and **106** were also exploited for the copolymerization of ethylene with MA and MMA. Here, the effect of binuclearity is even more evident since monometallic analogues are only minimally responsive to these monomers. Indeed, both catalysts afforded in good yield

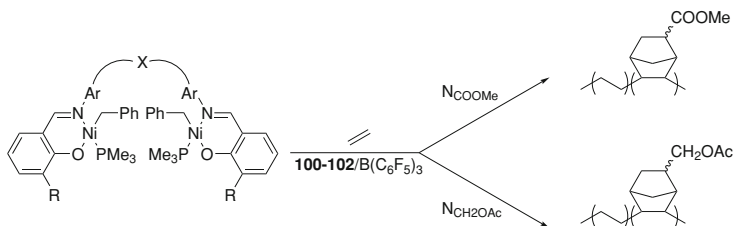


Fig. 2.35 Ethylene copolymers with functionalized norbornenes by binuclear bis-salicylaldiminato nickel catalysts

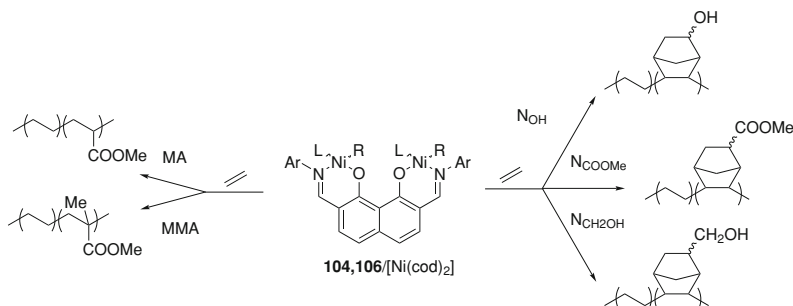


Fig. 2.36 Ethylene copolymers with MA, MMA, and functionalized norbornenes by naphthyl-oxydiiminato Ni(II) catalysts

P(E-*co*-MA) ($M_w = 6.3\text{--}6.7 \text{ kg mol}^{-1}$, $M_w/M_n = 1.6\text{--}1.7$, $T_m = 108 \text{ }^\circ\text{C}$) with an excellent incorporation of MA (11 mol%) and P(E-*co*-MMA) ($M_w = 7.9\text{--}8 \text{ kg mol}^{-1}$, $M_w/M_n = 1.4\text{--}1.7$, $T_m = 106 \text{ }^\circ\text{C}$) with MMA content of 8–9 mol%. The effective random copolymerization of E and (meth)acrylates was confirmed by fractionation, SEC, ^{13}C NMR, FT-IR, and DSC data.

The neutral nickel complexes **114–116** with asymmetric β -ketoiminato ligands activated by MMAO were reported to efficiently copolymerize ethylene with MMA (Fig. 2.37), though they behave as ethylene oligomerization catalysts in absence of MMA. As for ethylene homopolymerization substituents on N–O ligand strongly affect catalytic behaviour. Specifically strong EWG such as CF_3 allow for preparing P(E-*co*-MMA) copolymers with considerably high incorporation of MMA (until 17 mol%). Conversely, activity resulted higher when ancillary ligand was less electron deficient ($\text{R}^1 = \text{Ph}$; $\text{R}^2 = \text{Me}$). These copolymers possessed interestingly high molar masses, although polydispersity resulted somewhat broad.

Five membered chelated complexes **146–148** were investigated as catalysts for the copolymerization of ethylene with carbon monoxide (Fig. 2.38). Interestingly, the presence of EWG on the pyridyl ring on the N–O chelate ligand not only converts oligomerization catalysts into polymerization catalysts but also allow for obtaining polyketon-based material.

Catalyst **147** with the strong EWG nitro afforded the perfectly alternating P(E-*al*-CO) whereas the pyrazine-containing complex **148** yielded the blocky PE-*b*-P(E-*alt*-CO). By contrast, a weak donor group such as MeO promoted E oligomerization rather than E-*co*-CO copolymerization.

Nickel complexes with α -iminocarboxamide ligands were intensively investigated in the copolymerization of ethylene with functionalized norbornene derivatives N_{OH} and N_{OAc} [101] (Fig. 2.39).

Fig. 2.37 P(E-*co*-MMA) copolymers by β -ketoiminato Ni(II) complexes

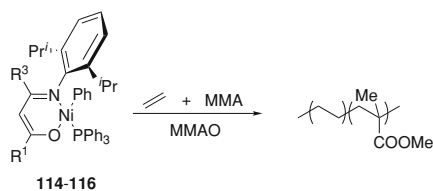
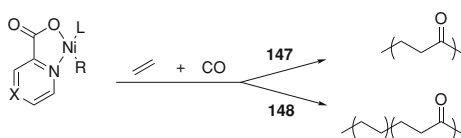


Fig. 2.38 Copolymerization of ethylene with carbon monoxide by pyridine carboxylato Ni(II) complexes



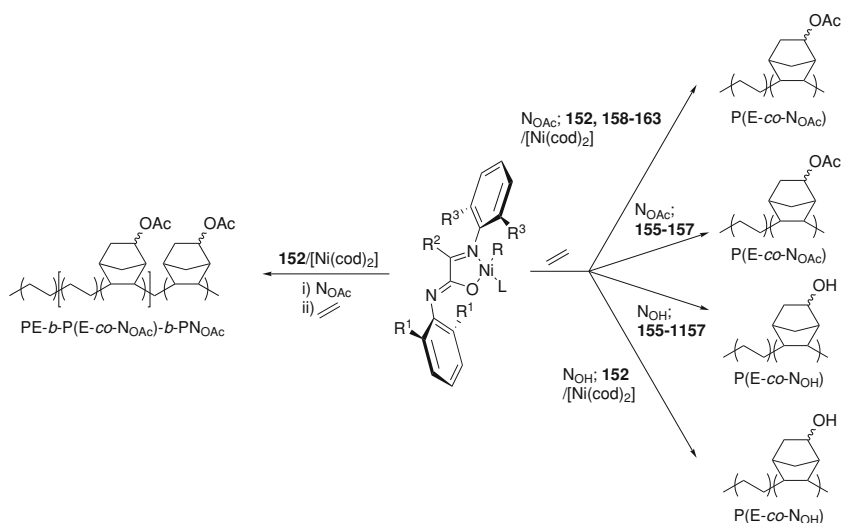


Fig. 2.39 Ethylene copolymerization with functionalized norbornenes by α -iminocarboxamide nickel catalysts

Complex **152** activated by $[Ni(cod)_2]$ as scavenger of PMe_3 yielded $P(E-co-N_{AC})$ copolymers containing 4–17 mol% of N_{AC} with excellent molar masses ($M_n = 30\text{--}110\text{ kg mol}^{-1}$). Very interestingly, catalyst **152** preserved the ability to promote the controlled polymerization of ethylene even in presence of N_{AC} as confirmed by linear time dependence of molar mass, that keep molar mass distribution somewhat narrow even after 90 min of reaction.

Also the hydroxyl-functionalized N_{OH} is readily incorporated in polyethylene backbone affording $P(E-co-N_{OH})$ copolymers with an incorporation of N_{OH} ranging from 5 to 18 mol% and possessing $M_n = 11\text{--}56\text{ kg mol}^{-1}$. Since hydroxyl functionality resulted more poisoning than acetyl group molar masses and activities were lower than those observed in $E-co-N_{AC}$ copolymerization. In addition controlled nature of copolymerization is absent, as revealed by the non-linear increase of molar masses with increasing reaction time as well as by the broader molar mass distributions.

Very interestingly, catalyst **152**/ $[Ni(cod)_2]$ was exploited to prepare $P(E-co-N_{AC})$ copolymers with decreasing content of polar monomer. Thanks to the controlled nature of copolymerization and through complete conversion of N_{AC} “polar–apolar” block-copolymers that show microphase separation were prepared [102].

Complexes **152**, **158–163**/ $[Ni(cod)_2]$ were exploited as catalysts for the copolymerization of ethylene with N_{AC} to investigate eventual steric and perturbative effects of group adjacent to imine (R^2), by keeping the same bulky 2,6- i PrC₆H₄ as aryl frameworks. Interestingly both activity and incorporation of comonomer are sensitive to this modification. Productivity increased with the increasing of the

bulkyness of alkyl groups as $i\text{Pr}$ (**160**) > $i\text{Bu}$ (**159**) > Et (**158**) > Me, whereas incorporation behaved oppositely. In the series of aromatic substituents, that is complexes **161–163** the higher electron withdrawing power the lower activity. Incorporation was less influenced though lower than the alkyl-substituted analogous.

Also complexes **156–157** with 2,6-lutidine and pyridine as neutral ligand, were demonstrated to act as single component catalysts for the copolymerization of ethylene with N_{OH} and N_{AC} yielding comparable results to phosphine-based analogous apart from molar mass distribution which was evidently affected by a less efficient activation [96].

2.4.4 Aqueous Olefin Polymerization

Neutral late transition metal complexes are more tolerant toward polar media than their cationic counterparts. Soon after their introduction, Ni(II) polymerization catalysts **1** and **2** were noted to display a certain stability toward small amounts of added water [39]. The use of water as a dispersing medium offers a unique combination of features, such as effective transfer of the heat of reaction, high polarity and formation of micelles. Moreover, polymerizations that can be carried out in aqueous emulsion give dispersions of submicron polymer particles (Fig. 2.40).

In 2001 Mecking gave the first full account on aqueous coordination polymerization of ethylene by neutral nickel(II) complexes **11**, **12** and by using $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})]$ as a phosphine scavenger [40]. A small amount of water or acetone was utilized to effectively add the water insoluble Ni(II) catalyst precursors or the phosphine scavenger, respectively. Polymer yields are lowered in water by comparison to conventional polymerization in organic solvents, while polymer molecular weights are noticeably higher compared to aqueous polymerization reactions with P–O chelate catalysts [103] (Table 2.3).

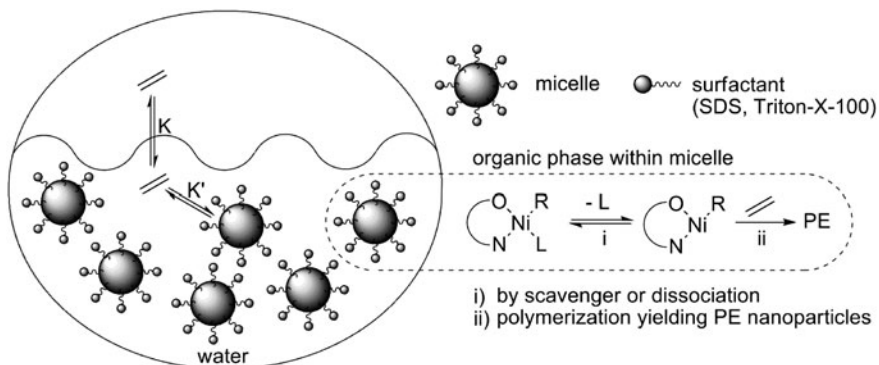


Fig. 2.40 Catalytic aqueous emulsion polymerization

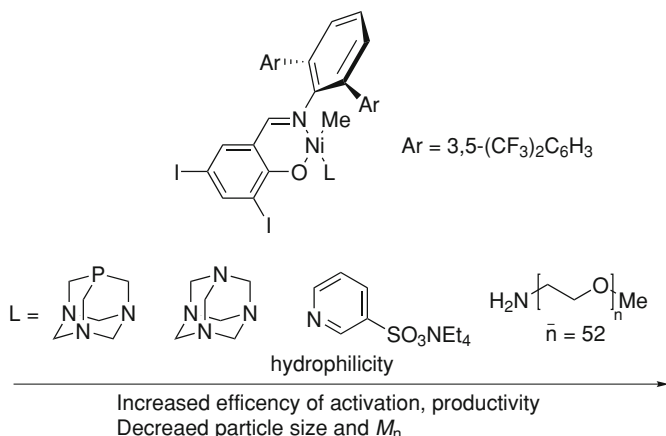
Table 2.3 Aqueous polymerization by catalyst **11**

Cat. no.	L	Reaction medium	<i>p</i> E (bar)	Solvent used for addition of cat.	T (°C)	TOF ^a	<i>M</i> _w (kg mol ⁻¹)	<i>M</i> _w / <i>M</i> _n
11	PPh ₃	H ₂ O	50	Pentane (10%)	70	50	410	4.1
11	PPh ₃	H ₂ O/acetone 50:50	50	/	50	40	18	1.5
11	PPh ₃	pentane	50	/	70	144	410	3.7
11	PPh ₃	Acetone	50	/	50	143	n.d.	n.d.
11	PPh ₃	Toluene	8	/	50	11	43	2.3
11	PPh ₃	Toluene	50	/	50	228	n.d.	n.d.
12	py	H ₂ O	50	Acetone (5%)	50	36	310	2.6

^a Kg PE mol cat⁻¹ h⁻¹

Water soluble complexes suited as catalysts precursors, which simplify the dispersions by removing the organic solvent in the initial catalyst system, are desirable for studies of the processes and of particle formation [104]. Four Ni-salicylaldiminato methyl complexes [(N-O)NiMe(L)], **61** and **67–69**, with various P- and N-coordinating water soluble ligands L (Fig. 2.41) were prepared by Mecking [105].

All complexes are soluble in toluene whereas **67–69** are insoluble in water; however, **69** is soluble in 2-propanol. In contrast, **61** is soluble in water. Polymerizations in aqueous systems were carried out in the presence of sodium dodecylsulfate (SDS) as a surfactant to stabilize polymer particles formed. Complex **67** with the water-soluble alkylphosphine PTA was inactive in aqueous suspension as well as in toluene solution due to the strong coordination of phosphine. Exposure of suspensions of the water-insoluble **68** to ethylene pressure (in the presence of surfactant to potentially stabilize polymer particles formed)

**Fig. 2.41** Effect of the stabilizing ligand on the efficiency and polymer particles in aqueous polymerization with salicylaldiminato nickel catalysts

afforded polymer suspensions. When **69** was introduced to an aqueous surfactant solution as a solution in 2-propanol, no visible precipitate was formed. Exposure to ethylene resulted in formation of polymer particles in the form of a latex, with large particle size.

These findings highlight that the size of polyethylene particles obtained by aqueous catalytic polymerization depends on the degree of dispersion of the catalyst in the initial reaction mixture. Catalyst **61** revealed to be a very performing catalyst producing in 3.5 h, at $T = 20\text{ }^{\circ}\text{C}$ and $p\text{E} = 40\text{ bar}$, 9.4 g of PE in form of latex ($M_n = 8.8\text{ kg mol}^{-1}$) with particle size of 230 nm.

Electron-withdrawing substituents in the bidentate N, O- or P, O-coordinating ligand, substantially increased the polymerization rates of Ni(II) complexes as shown by Brookhart et al. for enolatoimine complexes **117–120**, while electron-poor phosphinoenolate complexes afforded higher molecular weight polymer. Even though with increasing electrophilicity of the metal center, an increased reactivity and sensitivity toward water was anticipated in 2007 Mecking synthesized a series of neutral Ni(II) complexes based on enolatoimine ligands with strongly electron-withdrawing trifluoromethyl and trifluoroacetyl groups that were studied as catalyst precursors for ethylene polymerization [66]. Despite the electron-deficient nature of the metal centers, which can enhance deactivation processes such as hydrolysis or coordination of water, they were very active in aqueous emulsions affording polyethylene dispersions. Studies of different catalyst precursors, $[(\text{N}-\text{O})\text{NiMe}(\text{L})]$ with $\text{L} = \text{pyridine}$ or PPh_3 , or in situ prepared catalysts $[(\text{tmeda})\text{-NiMe}_2]/\text{ketoenamine}$, show that exchange of the coordinating ligand L is a critical step for the electron-poor Ni(II) complexes studied and likely is one limiting factor for catalyst activities.

The pyridine complexes **126** and **127** were dissolved in a small amount of toluene and the solution miniemulsified in aqueous SDS solution. Exposure to ethylene in a pressure reactor afforded stable dispersions. This demonstrates that in spite of the strongly electron-withdrawing nature of the enolatoimine ligands in the catalysts studied, catalyst stability toward water is sufficient to carry out polymerization in aqueous systems. Catalyst **127** at $70\text{ }^{\circ}\text{C}$ gives an average activity of $1.9 \times 10^4\text{ mol C}_2\text{H}_4\text{ mol Ni}^{-1}$. This competes with the highest activities reported for neutral Ni(II) salicylaldiminato complexes, the only ones reported before to afford polyethylene dispersions of high molecular weight material ($M_n = 10\text{ kg mol}^{-1}$) [106]. Also the phosphine complex **128** is suited for polymerization in aqueous medium by using $[\text{Ni}(\text{cod})_2]$ as a phosphine scavenger with a TOF of $9,500\text{ mol C}_2\text{H}_4\text{ mol Ni}^{-1}\text{ h}^{-1}$ and $M_w = 24\text{ kg mol}^{-1}$. The phosphine complex **128** is active in the absence of a phosphine scavenger in non aqueous systems. Thus, by comparison to polymerizations in nonaqueous systems, activity is reduced 5–10-fold probably due to the disactivation of a part of the catalyst precursor upon preparation of the miniemulsion or in the early stages of the polymerization experiment. TEM micrographs show the particles to be spherical with particle size ranging from 91 to 544 nm.

The substituents on the N-bound aryl group ($\text{N}-\text{C}_6\text{H}_3\text{R}_2$) affect the degree of branching of the polymer formed and in turn its crystallinity and melt temperature.

For $R = {}^i\text{Pr}$ a total degree of branching of 40–50 is observed ($T_m \sim 97^\circ\text{C}$, crystallinity $\sim 35\%$), while for $R = 3,5\text{-(F}_3\text{C)}_2\text{C}_6\text{H}_3$ ca. 25 branches/1,000 carbon atoms ($T_m \sim 110^\circ\text{C}$, crystallinity $\sim 45\%$) are found.

There is a strong interest in developing more active neutral Ni(II) complexes, being catalyst activity an issue in polymerization with these systems in general and in aqueous systems in particular. Since binuclear complexes can afford greater activity, higher molar masses and comonomer incorporation than the mononuclear analogue Mecking tested the binuclear complexes **96–99** in the ethylene polymerization in aqueous emulsion obtaining polyethylene dispersions. These binuclear pyridine complexes are very robust, in fact they are active over the entire temperature range studied, 20–70 °C, as single-component catalyst precursors, without the necessity of an activator and with a maximum of productivities up to $184 \times 10^3 \text{ C}_2\text{H}_4 \text{ mol Ni}^{-1} \text{ h}^{-1}$ at 50 °C and pE = 40 bar. A broad distribution of polymer particle size with approximately a circular circumference was obtained. In addition to the pyridine complexes, the complex **96** of the less strongly coordinating tertiary amine tmeda was studied. In this case an activity was observed at a low polymerization temperature of 25 °C with a productivity of 2,500 mol $\text{C}_2\text{H}_4 \text{ mol Ni}^{-1} \text{ h}^{-1}$ and a very high ($M_n = 232 \text{ kg mol}^{-1}$) molecular weight and linear polyethylene. Polymer molecular weights and melting points are similar to those obtained in nonaqueous polymerizations under identical conditions. However, as for mononuclear complexes, productivities in aqueous emulsions are decreased by comparison to polymerization in organic solvents.

2.5 Mechanistic Aspects

2.5.1 Mechanism of Ethylene Homopolymerization

Fundamental steps involved in ethylene polymerization catalyzed by N–Z containing Ni and Pd catalysts are depicted in Fig. 2.42. Generation of the active species, previously discussed, yields the hydrocarbyl complex with a vacant coordination site for the incoming olefin. Polymerization propagates via chain migration through four-centered transition state and product of insertion resembles the starting active species with a new vacant coordination site available for the further olefin coordination and insertion. Frequent termination pathways involve $\beta\text{-H}$ elimination and $\beta\text{-H}$ transfer to the monomer. Both lead to chain releasing with generation of a new active species. A feature of these catalysts is the formation of chain branches as a result of consecutive $\beta\text{-H}$ elimination, rotation, and reinsertion reactions; the longer the chain walks the longer the branches.

In-depth mechanistic and theoretical works were focused on the cationic diimine complexes of nickel and palladium. NMR studies revealed a unique feature of these systems, the catalyst resting state is the alkyl ethylene complex. This is in clear contrast with early transition metal catalysts whereby such species are

trans to the nitrogen donor are lower. Since the insertion of an ethylene unit changes the configuration of the chain with respect to the salicylaldiminato ligand, isomerization occurs at the π -complex stage so that insertion could proceed through the lower energy transition state. Accordingly, the lowest energy pathway for insertion proposed is depicted here with continuous arrows.

Interestingly, the β -H transfer mechanism for the termination was found to be energetically more favorable than the β -H elimination mechanism. The termination barriers found were generally higher than the insertion barriers. A comparison of the results obtained by varying the substituents on the catalyst backbone led to the conclusion that while influence of electronics on catalyst activity could not be easily predicted the addition of bulky substituents on the catalyst backbone should enhance catalyst activity.

Subsequently, combined DFT/stochastic studies were undertaken on the mechanism of ethylene polymerization catalyzed by a neutral Ni-anilintropone catalysts. Chain propagation and isomerization as well as influence of reaction conditions on the branching formation were investigated. Similarly to the case of nickel-salicylaldiminato catalysts the activation barriers for the insertion of ethylene in complexes with the alkyl group trans to the oxygen donor were found higher than those encountered in *cis/trans* isomerization. Interestingly, stochastic simulation allowed for establishing temperature and pressure dependence of the polymer microstructure. In agreement with experimental evidences the model predicts a decrease with the number of branches with the increase of pressure. Temperature dependence behaves oppositely as a result of an increase in secondary insertions with the temperature.

To get a full mechanistic picture of a typical neutral catalyst system an elegant and in-depth NMR study of ethylene polymerizations catalyzed by the anilintropone complexes was reported by Jenkins and Brookhart [107]. Detailed information concerning the chain propagation process, the barrier to ethylene insertion, the nature, and dynamics of the intermediate Ni alkyl complexes, and the chain transfer and catalyst decay processes were obtained.

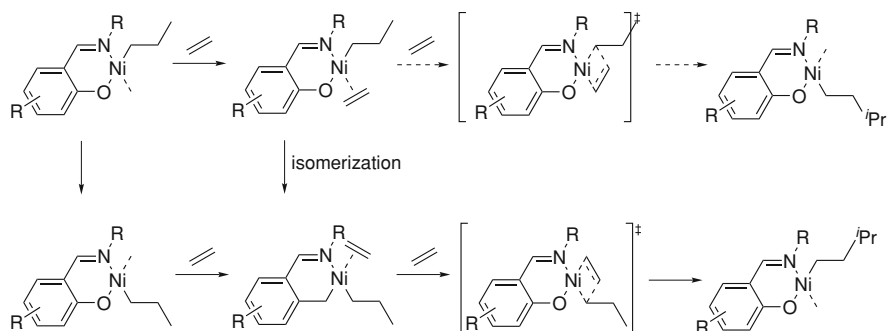


Fig. 2.43 The lowest (continuous) and highest (dashed) energy pathways for the insertion of ethylene at nickel center in salicylaldiminato catalysts calculated by DFT

The rate of insertion of ethylene into the Ni-phenyl bonds of both unsubstituted and aryl-substituted of anilinetropone nickel(II) complexes was monitored by low-temperature NMR spectroscopy. The ethylene chain growth to form, initially, the corresponding $[\text{Ni}(\text{L})(\text{PPh}_3)(\text{CH}_2\text{CH}_2\text{Ph})]$ ($\text{L} = \text{M2}, \text{M13-16}$) complexes, was determined by monitoring the change in concentrations of starting complexes. First-order rate constants were measured as a function of temperature and ethylene concentration.

Even at high ethylene concentrations, only PPh_3 complexes were observed (no ethylene complexes were detected). As expected, rates accelerate with temperature, increasing about an order of magnitude between -10 and 10°C . Insertion is dramatically inhibited by phosphine concentration. Thus, it was concluded that for these systems, the catalyst resting state(s) are an equilibrium mixture of phosphine and ethylene complexes (Fig. 2.44). Nevertheless, at high ethylene pressures, the equilibrium is shifted nearly completely to the side of the ethylene complex and TOF becomes independent of ethylene pressure (saturation conditions).

The barriers to migratory insertion in $(\text{N-O})\text{Ni}(\text{R})-(\text{C}_2\text{H}_4)$ complexes, from measurements of TOFs under saturation conditions, were determined to lie in the range of $16\text{--}17\text{ kcal mol}^{-1}$, that is only about $2\text{--}3\text{ kcal mol}^{-1}$ greater than those observed for cationic diimine complexes.

The intermediate alkyl complexes have α -agostic interactions with dynamic behavior similar to the cationic alkyl diimine complexes. The barrier to β -H elimination and reinsertion is estimated in ca. 17 kcal mol^{-1} . Free energy barrier to nickel-carbon bond rotation in these complexes occurs with a barrier of $11.1\text{ kcal mol}^{-1}$. These isomerization processes account for branched polyethylenes generated from these catalysts and resemble those previously observed with diimine catalysts.

Thermolysis of hexyl complex **182** generates the nickel hydride complex and 1-hexene via β -H elimination, through two pathways, one (dominant) independent of phosphine concentration and one involving reversible loss of phosphine, and thus inhibited by PPh_3 . This process is a model for chain transfer and clearly explains why polymer molecular weights decrease with increasing phosphine

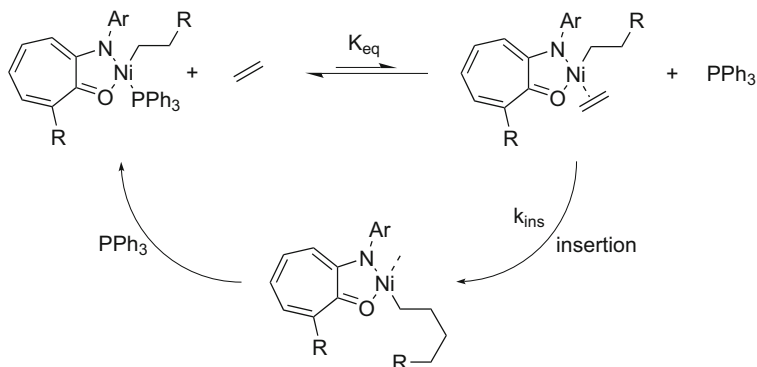


Fig. 2.44 Ethylene polymerization catalyzed by Ni-anilinetropone catalysts

concentration. The rate of propagation is retarded by increasing $[\text{PPh}_3]$, while the rate of chain transfer is unchanged, resulting in an increase in $R_{\text{ct}}/R_{\text{prop}}$. Since chain transfer to monomer would exhibit a rate inhibition equal to that for R_{prop} with added PPh_3 it was concluded that the major chain transfer route is a simple β -elimination process, and not chain transfer to monomer.

At much slower rates, reductive elimination of the free ligand occurred from the hydride complex, (Fig. 2.45) and is inhibited by added phosphine. Catalyst decay under polymerization conditions was shown to occur by a similar process to generate free ligand and a bis-ligand complex formed by reaction of free ligand with an active catalyst species (Fig. 2.46).

Recently, Mecking [108] reported in depth mechanistic studies of the novel (dmsO)-coordinated complex **70**. Such complex resulted to be a suitable precursor for mechanistic studies of deactivation routes of neutral Ni(II) catalysts. Activation of **70** could be directly observed using dmsO as a solvent, by ^1H NMR spectroscopy. Interestingly, a minor but sufficient portion of **70** was transformed into the hydride containing active species by insertion of ethylene and subsequent elimination of propylene.

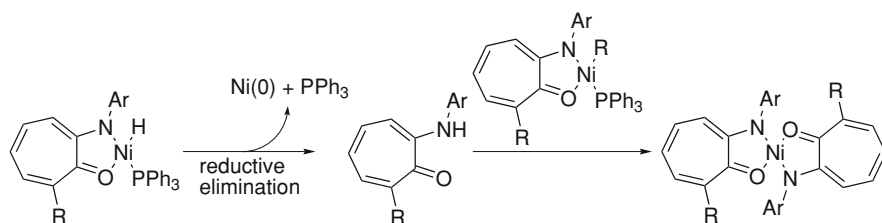


Fig. 2.45 Catalysts deactivation for anilinetropone nickel catalysts

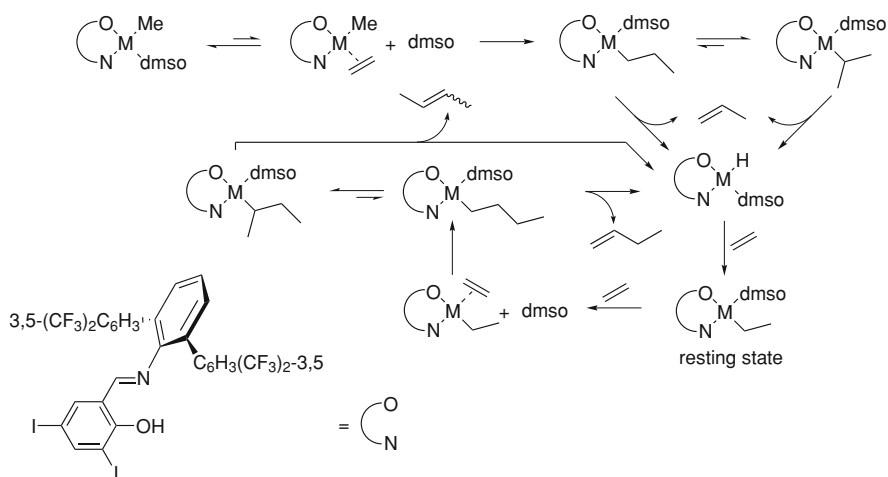


Fig. 2.46 Mechanism for ethylene polymerization from NMR studies of neutral $[\text{Ni}(\text{A14})\text{R}(\text{dmsO})]$ species

Surprisingly, catalyst resting state is the ethyl complex **72** that can undergo two different processes: (1) *cis/trans* isomerization of alkyl and dmsol in respect to the position of donors in salicylaldiminato ligand and (2) exchange of α - and β -carbon of ethyl group β -H, rotation, and reinsertion. Catalytic dimerization of ethylene to 1- (15%) and 2-butenes (85%) was observed. Isomer ratio suggests secondary butyl-Ni complex as thermodynamically favoured.

To get insights on how this system behaves in presence of polar reagents, the reactivity toward water was examined. Added D₂O revealed that water does not significantly coordinate to the metal center. Hydrolysis of the Ni–Me bond of the catalyst precursor is evidenced by the formation of CH₃D. Conversely, no hydrolysis of the higher Ni–C_nH_{2n+1} ($n > 1$) occurring during chain growth was observed, suggesting that hydrolysis of Ni-alkyl species is a minor decomposition pathway. More remarkably, the significant deactivation was found to be the reductive elimination of alkanes by reaction between alkyl and hydride containing species as well as by reaction of two Ni–Me catalyst precursors yielding ethane. This is in line with the previous Grubbs' suggestion that bulky substituted salicylaldiminato ligands hinder catalyst decomposition [109]. These studies demonstrated for the first time that bimolecular elimination of alkane from reaction of Ni-alkyl and Ni-hydride species is a possible deactivation route for neutral nickel catalysts. This provides a rationale for catalyst design and for an appropriate choice of reaction conditions that provide site isolation.

2.5.2 Mechanism of Copolymerization of Ethylene with Polar Monomers

Neutral nickel(II) catalysts are attractive for their functional group tolerance and potential in copolymerization of vinyl polar monomers. As already pointed out, cationic Pd-diimine catalysts pioneered by Brookhart, allow the coordination–insertion copolymerization of ethylene with polar vinyl monomers such as MA and VA. Low-temperature NMR studies of reactions of cationic palladium R-diimine complexes with ethylene and methyl acrylate revealed all of the critical intermediates spectroscopically and allowed in depth mechanistic understanding. They are formed by chelating coordination of the carbonyl group of an inserted MA unit. Acrylate insertion occurs predominantly in a 2,1-fashion, yielding chelate species of general formula [Pd(N–N)(κ^2 -C,O-CHRC(=O)OMe)] in which the carbonyl group of the inserted MA is coordinated to Pd yielding a strained four-membered chelate ring. Subsequent β -H eliminations and readditions expand the ring stepwise to the six membered chelate complex, which is the catalyst resting state. Opening of these chelates by coordination of incoming monomer to form the corresponding olefin complexes is the turnover-limiting step during copolymer chain-growth [110, 111].

The relative E/MA ratios of incorporation into the copolymers are governed by both the equilibrium ratio of the alkyl ethylene and alkyl MA complexes and their relative rates of migratory insertion. Even if the rate of migratory insertion of MA

is somewhat faster than that of ethylene at low temperature, there is a great preference for ethylene binding to the electrophilic Pd center is over that of the electron-deficient olefin, MA. This implies use of very large $[MA]/[E]$ ratios to achieve significant incorporation of MA into the copolymer. As a consequence, the overall rate of polymerization decreases due to increased concentrations of the chelate complex.

Conversely, most attempts to copolymerize ethylene with MA with Ni-diimine catalysts were unsuccessful. Theoretical investigations by gradient-corrected DFT theory revealed that the main difference between Ni and Pd is that *O*-bonding mode of MA due to the higher oxophilicity of Ni, owed namely to steric reasons rather than to the orbital interaction [112]. They suggested that copolymerization would be possible under harsh conditions. Indeed some Ni-diimine-based systems were reported to effectively copolymerize E with MA at high temperatures (120 °C) and very high pressure (340 bar). These conditions appeared to favour the dissociation of the carbonyl coordination of MA from the electrophilic nickel centre. Very interestingly while ethylene-MA copolymers obtained with cationic Pd diimine catalysts are highly branched due to extensive chain walking, Ni complexes give linear ethylene-MA copolymers.

It was foreseen that to avoid problem of the *O*-binding of MA to oxophilic cationic Ni catalysts the use of anionic ligands would enhance the preference for the π -coordination and favour the ethylene MA copolymerization [112, 113].

These results encouraged extensive studies of novel neutral nickel(II) olefin polymerization catalysts [97, 114, 115]. They are much more stable to protic and aqueous media and the variety of catalysts developed with different ligands allows to vary the microstructures and crystallinities of resulting polymers in a controlled fashion over a wide range. However, although the numerous polymerization studies, copolymerization of ethylene (or 1-olefins) with polar vinyl monomers, like MA, to high-molecular-weight copolymers employing neutral Ni(II) precatalysts is limited from either low activity or rapid catalyst deactivation.

Recently, a comprehensive NMR study of two neutral nickel complexes **71** and **72** provided insights into the reactivity of active neutral Ni(II) species toward polymerization of polar vinyl monomers (Fig. 2.47). The two complexes were found to be well-defined model compounds for these studies and allowed direct observations of organometallic species and decomposition products originating from insertion of polar vinyl monomer into the key intermediates.

MA insertion into the Ni–H bond of **71** was monitored at $T \geq -40$ °C by NMR spectroscopy. MA readily inserts into Ni–H bond as well as into Ni-alkyl species with exclusively regiospecific 2,1-insertions even at low temperature (-30 °C). A weak, but distinct, chelating interaction of the O-atom of the carbonyl group with the metal center after insertion was demonstrated at low temperature, in agreement with a geometry-optimized structure calculated by DFT.

Exposure of the hydride **71** to equal amounts of ethylene and MA resulted in the formation of MA and ethylene insertion products in a 9:1 ratio, which demonstrated that both monomers can effectively compete with each other for coordination and insertion. Thus, a prerequisite for their copolymerization was fulfilled.

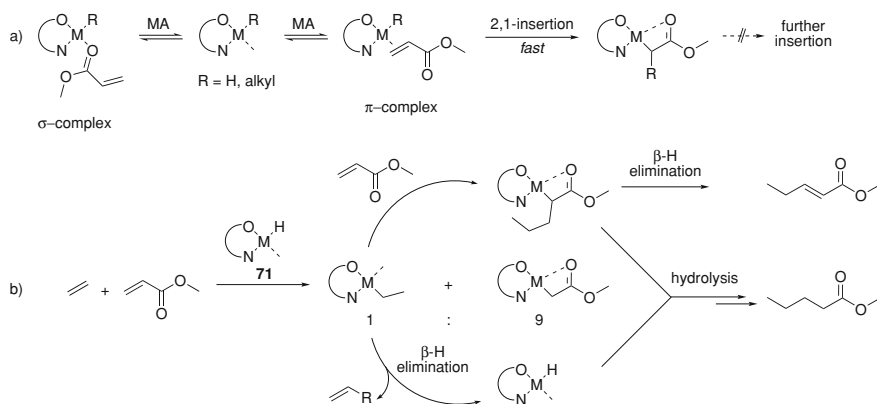


Fig. 2.47 Reactions of complex **71** with ethylene and MA

However, although the product of insertion is stable in the absence of residual Ni–H species at low temperatures, it is subject to rapid bimolecular elimination of the functionalized alkyl moiety in the presence of free **71**. Moreover, at 0 °C β -H elimination occurs to such an extent and decomposition from solutions initially not containing the hydride takes place. Exposure of the higher Ni-alkyl complex to MA in the presence of excess ethylene results in the immediate formation of methyl pentanoate as the ultimate decomposition product.

Interestingly, while the Ni-Et species is practically stable toward hydrolysis at 55 °C [107, 108] the analogous R-carbonyl substituted metal alkyl originating from 2,1-insertion of MA is subject to rapid hydrolysis at room temperature in agreement with the previous studies on the organic decomposition products of the reaction of a Ni-phenyl complex **5** with MA [116].

VA inserts less readily than MA into the hydride complex **71**. Insertion occurs at 0 °C, yielding both the kinetic 1,2-insertion product and the thermodynamically favored 2,1-insertion product. NMR data and a theoretical study indicate an interaction of the carbonyl O-atom with the nickel atom, structurally similar to the MA insertion product. Decomposition occurs by β -acetate elimination even at low temperatures.

Qualitatively, the observed reactivity of VA toward the neutral hydride and alkyls complexes studied parallels observations with cationic Ni(II) diimine complexes [117].

2.6 Summary and Conclusions

Group 10 metal complexes with mixed ligands based on nitrogen (N–Z) for olefin polymerization catalysis in academic articles have been comprehensively reviewed. Olefin, namely ethylene, homopolymerization and copolymerization of

ethylene with functionalized norbornenes, functionalized α -olefins, and polar vinyl monomers have been considered. It is clear that while palladium and P–O ligands were discovered first and dominate ethylene copolymerization with CO and the SHOP process, nickel and N–O chelates prevail in the new classes of late-transition metal complexes with mixed chelating ligands for olefin polymerization catalysis. This is related to the higher insertion barrier in palladium diimine catalysts when compared to the analogous nickel complexes. The nickel P–N based catalysts reported so far reveal a greater stability and a greater tendency to chain walking (branches on branches) than diimine catalysts, but there is no clear tendency in the few examples since small changes in the substituents or subtle variations in the structure give dramatic differences in the catalytic behaviour. Palladium catalysts with P–N ligands are low active and tend to decompose, as they seem to do those with N–S ligands.

Most ligands in nickel complexes such as salicylaldimine, anilinetropone, enolatoimine, and other ligands are anionic and feature steric bulk to achieve high molecular weights. Thanks to the combination of steric and electronic factors on the substituents and the dissociation ability of the stabilizing ligand ($\text{dmsO} > \text{MeCN} > \text{py} > \text{PR}_3$) most behave as single component catalysts. Addition of a cocatalyst or of a scavenger as $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ni}(\text{cod})_2]$ enhances the activity. In phosphine complexes insertion is inhibited by phosphine concentration since the resting state of these systems is the phosphine complex. In NMR studies of anilinetropone catalyst in the presence of ethylene the resting state(s) was demonstrated to be an equilibrium mixture of phosphine and ethylene complexes.

Regarding the olefin polymerization there is a temperature and pressure dependence of the polymer microstructure, namely the degree of branches. A decrease of branching occurs with the increase of pressure, while the temperature dependence is opposite, due to an increase in secondary insertions with the temperature.

More relevant for the design of catalysts is the selection of the substituent on the chelate scaffold. The salicylaldiminato complexes of Ni(II) are the best studied of these systems since, having many sites available for substitution, they allow appropriate tailoring of the catalyst. Depending on substituent variation it is possible to tune activities, molar masses, and branching. High activity can be reached.

The N-aryl ring lies roughly perpendicular to the square plane of the molecule, increasing the steric bulk of ortho substituents on this ring increases the catalyst productivity, M_w , and linearity of PE. Electron withdrawing or donating substituents on N-terphenyl moieties have remote dramatic effects on branching, crystallinity and molar masses: linear, semicrystalline or highly branched, amorphous polymers can be prepared. Often branches increase at the expense of molecular weight. Electron withdrawing substituents on the phenoxide ring also increase the productivity. Thus, an increased electrophilicity of the Ni center, brought about by electron withdrawing groups in the N–O ligand increases the polymerization rates. Bulky substituents adjacent to the phenoxide group increase catalyst lifetime by slowing or preventing decomposition to the corresponding bis(salicylaldiminato)

Ni complexes. The design and synthesis of binuclear Ni(II) aldiminato complexes showed cooperativity effects leading to more linear PE with very high activity and molar masses.

Similar effects of substituents adjacent the oxygen of the chelate ring or on the N aryl groups are observable in other families of six membered ring ligands as PymNox and enolatoimine complexes, which are also very active for ethylene polymerization.

Steric and electronic effects have similar influence also in complexes with five membered ring ligands. In particular the anilinetropone complexes feature PE with highest activity and very high molar masses, while those based on α -iminocarb-oxamide allow to obtain living systems at 20 °C, when activated with [Ni(cod)₂].

Thus, these Ni catalyst systems are capable of introducing over 50 branches/1,000 C into the polymer chain, yielding polymers with lower melting points than those produced by their group 4 catalysts. A controlled degree of branching is desirable in polyolefins to depress the glass transition and melting temperatures, thus improving processability. However, they typically exhibit PE with lower molecular weight than catalysts industrially used.

The high activity of some of these neutral late transition metal catalysts, which are active in the presence of polar additives with only minor reduction in activity, makes them interesting for the synthesis of polymer dispersions by polymerization in aqueous systems. Although, with increasing electrophilicity of the metal center also reactivity and sensitivity toward water increase. Very interesting results were achieved with the most active complexes, especially those based on enolatoimine and ditopic salicyladimines. Very high TOF and molar masses were obtained even though productivities in aqueous emulsions are decreased by comparison to non aqueous polymerization.

The main interest in these systems arise from the need to incorporate small amount of monomers containing polar groups to endow polyolefins with additional physical and chemical characteristics. Indeed, the neutral salicylaldiminato based nickel catalysts copolymerize ethylene with a variety of functionalized norbornenes such as 5-norbornen-2-ol and 5-norbornene-2-yl acetate, and functionalized α -olefins, showing the functional-group tolerance of these neutral catalysts. Incorporation of functionalized norbornenes with bimetallic complexes is four times that with mononuclear analogues. Random and block copolymers between ethylene and functionalized norbornenes have been achieved with α -iminocarb-oxamide complexes.

More challenging still is copolymerization with polar vinyl monomers. There are few examples of linear copolymers with acrylates by mononuclear (N–O)Ni complexes. Recent studies have demonstrated that the challenging nature of these copolymerizations arises from the low reactivity towards olefin insertion of an α -carbonyl substituted metal alkyl combined to the particular susceptibility of functionalized olefin insertion products to specific bimolecular deactivation reactions and hydrolytic pathways. Site isolation (and strictly inert conditions), however, enhancing the reactivity of the functionalized olefin insertion product for following insertions seems to be necessary.

More interesting are the results with binuclear (N–O)Ni complexes. The cooperative bimetallic catalytic interactions lead to increased polar comonomer enchainment selectivity for functionalized monomers and especially for acrylates (ten, one hundred times that from monometallic complexes). The selectivity of the bimetallic systems for higher comonomer incorporation, as well as different branch content, affords substantially altered polymer microstructures, with lowered melting points and greater solubility. Furthermore, the bimetallic catalysts exhibit significantly higher activities than the monometallic catalysts in the presence of polar solvents, while concurrently achieving higher molecular weights. This feature permits using less rigorously dried media for polymerization while preserving the desired product microstructure. Finally, the cooperative effects between group 10 catalytic centers, not only substantially enhance the catalyst/polymer properties that have made the monometallic analogues of interest, but also expand the range of polymerizations possible.

In conclusions, progress in design and synthesis of neutral nickel catalysts and understanding of the factors that regulate the reactivity towards olefin and polar monomers give promise to address the issue of introducing functional groups into aliphatic polyolefin backbones. It is expected that even though modern palladium complexes based on P–O ligands give very attractive copolymers with polar monomers, economical and environmental concerns related to palladium catalysts will encourage further efforts in the design and developments of nickel and other more environmental friendly catalysts.

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