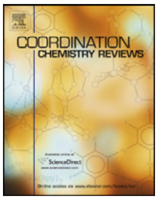
Coordination Chemistry Reviews 255 (2011) 2785–2809

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Catalytic and coordination facets of single-site non-metallocene organometallic catalysts with N-heterocyclic scaffolds employed in olefin polymerization

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Contents

ARTICLE INFO

Article history:
Received 15 December 2010
Accepted 26 April 2011
Available online 5 May 2011

Keywords:
Non-metallocene
N-heterocyclic
Organometallic
Olefin polymerization
Ring opening metathesis polymerization
Transition metal catalyst

ABSTRACT

This review discusses the principles underlying mononucleating N-heterocyclic ligand design, selectivity of metal centers, preparation of organometallic catalysts with a N-heterocyclic backbone, and their catalytic activity in olefin oligo/polymerization. A vast number of N-heterocyclic organometallic compounds have been applied for the polymerization on account of their modest cost, low toxicity, and the large availability of transition metals in stable and variable oxidation states, which makes them versatile precursors for these reactions. The main points of focus in this review are the key advances made over more the past 25 years in the design and development of non-metallocene single-site organometallic catalysts bearing different N-heterocyclic scaffolds as a backbone. These catalysts are applied as precursors for the transformation of ethylene, higher α-olefins, and cyclic olefins into oligo/polymers. Emphasis is placed on the architecture of ligand peripheries for tuning the formed polymer properties and the consequences on product formation of different alkyl or aryl substituents directly attached to the metal center in a N-heterocyclic ligand system.

1. Introduction

The crucial properties of organometallic catalysts for olefin oligo/polymerization include the nature of the metal ions and the three-dimensional orientation of the ligands and positions of suitable alkyl or aryl substituents. This understanding has motivated the synthesis of novel mono-, bi-, and polynuclear organometallic catalysts for the production of desired polyolefins [1–3]. Non-metallocene organometallic catalysts encompassing N-heterocyclic scaffolds are employed in the hope that similar synergistic effects will occur as in metallocene-based catalysts, where the metal center is directly linked to an aromatic ring system. In this stream, many organic aromatic N-heterocycles have been employed as backbone synthons in ligand design with defined sub-

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doi:10.1016/j.ccr.2011.04.013

stituents at appropriate positions on the heterocycles [4,5]. Very few articles are available in the literature on organometallic binuclear catalysts designed specifically for olefin oligo/polymerization, in which both metal centers are separated by a bridging unit present in the heterocycle or by aliphatic/aromatic spacers. A variety of N-heterocycles can be exploited in the design of ligands for olefin oligo/polymerization because of their potential chelating properties towards electropositive metal atoms/ions to form stable catalysts. Very recently, non-metallocene single-site late transition metal catalysts have attracted attention in studies on the implications of electronic and steric effects originating from ligands on the oligo/polymerization of olefins [6]. Recent studies in this area using N-heterocycles such as pyridazine, pyrazole, and pyridine have encountered diverse and difficult challenges. Pyridine, acridine, pyrrole, and phenanthroline have been extensively studied for use in monometallic catalysts and pyrazole, pyridazine, and phthalazine, for bimetallic catalysts for olefin oligo/polymerization, with various substituents. These heterocyclic compounds are an important class of nitrogen heterocycles characterized by one or two nitrogen heteroatoms in an unsubstituted parent compound. The lone pair electron on the heteroatom may not be involved in the delocalization into the aromatic pi-electron system; hence, it acts as an organic base with properties similar to tertiary amines. Nitrogen heterocycles can undergo protonation, alkylation, acylation, and N-oxidation at the heteroatom like tertiary amines because of their basic character. The heteroatom is more electronegative in nature and has a strong tendency to donate the electron lone-pair to electropositive organometallic precursors under appropriate reaction conditions to form stable coordination compounds or complexes. The extent of nitrogen denticity depends on the nature and position of substituents on the heterocyclic ring system as well as the nature of the accepting atom/ion. For instance, in pyridine, electron-withdrawing groups at the *ortho*- and/or *para*-positions affect chelation by increasing the chance of back-bonding rather than the usual nitrogen lone-pair coordination. Conversely, electron-donating groups at the said positions enhance chelation from nitrogen and form stable coordination compounds of the desired compositions. However, the effect of substituents at the *meta*-positions is opposite to that at the *ortho*- and *para*-positions. These substituents are responsible for obtaining definite electronic and steric modulations in the ligand systems, which is a major consequence in getting the desired oligo/polymer in olefin oligo/polymerization by using single-site non-metallocene organometallic catalysts with defined substitutions on the heterocycles [7,8].

Another important corollary is mainly from the nature of metal atoms/ions, which collectively offer different properties to catalysts compared with their metallocene counterparts. In this review, we attempt to correlate the recent discoveries and developments in non-metallocene single-site organometallic catalysts bearing aromatic N-heterocyclic scaffolds for use in the production of oligo/polymers from different olefin monomers, ranging from simple α-olefins to conjugated cyclic olefins. Meticulous attention has been paid to the effects of alkyl-metal and aryl-metal catalysts on the rate and yield of oligo/polymerization in comparison with their metallocene counterparts under given reaction conditions. An additional group of important olefin oligo/polymerization organometallic catalysts was developed by the incorporation of a suitable organic or inorganic support such as carbon nanotubes, silica, and alumina [9–11]. Catalysts of this type are more stable than those that are unsupported, and even more insight into this field of research is needed as applications and requirements of these catalysts continue to multiply with particular pressure from commercial interests [12,13].

Over the last decade, increased interest in the development of selective oligomerization and polymerization catalysts has led to a diverse array of catalytic systems based on transition metal complexes, mainly using metallocenes. On the other hand, initial transition metal systems relying on ligands based on mono-Cp motifs linked to arenes and non-metallocene compounds without any metal–carbon linkage have garnered interest in recent studies. However, the importance of systems encompassing a non-metallocene organometallic core with a N-heterocyclic backbone has not been the main focus of any compilation. In this review, the array of successful non-metallocene organometallic transition metal catalysts (groups III–X) based on mononucleating ligands encompassing a N-heterocyclic backbone is discussed with different donor combinations such as NNN, NNO, ONO, PNP, NN, NP, NS, and NO. Synthetic, structural, spectroscopic, X-ray crystallographic, and computational investigations have been performed to gauge the catalytic significance of single-site non-metallocene catalysts bearing N-heterocyclic scaffolds such as pyrazole, pyrrole, imidazole, oxazole, thiazole, benzimidazole, indole, isoindole, pyridine, pyrazine, pyrimidine, and so on, in olefin oligo/polymerization.

2. Scope

The present review focuses on recent developments in the field of olefin polymerization using non-metallocene organometallic catalysts with N-heterocyclic hubs. This is a fairly large section of catalysis that covers the polymerization of simple α-olefins to conjugated cyclic olefins; hence, an attempt is made to consider data even from patents available from online patent databases. The scope is limited to explanations of N-heterocyclic ligands that provide suitable architecture for the ligation to form desired catalysts. In the elucidation section, triazole and tetrazole derivates are excluded as they were not generally used in the formation of active catalysts for the said reactions. Similarly, heterocyclic compounds encompassing more than one type of heteroatom, such as thiadiazole and oxadiazole, are also excluded. Late transition metal catalysts composed of copper or zinc are usually not active for olefin polymerization, and so only those few that are active are included. Ligand and catalyst syntheses, structures, activities towards olefin polymerization, and related mechanisms are discussed, as well as the consequence of these factors on the structures of the resulting polymers. Subjects specifically included are ethylene and norbornene polymerization catalyzed by organometallic catalysts with early transition metals. There have been several recent general ideas in the area of olefin polymerization; hence, there are numerous studies taking place in both academia and industry. A considerable number of additional reviews [14–19] are available in the literature on olefin polymerization with different catalysts and activators [20]. Here, we have attempted to collate the available information on olefin polymerization by non-metallocene organometallic catalysts with N-heterocyclic scaffolds.

Early transition-metal catalysts, such as Ziegler-Natta catalysts, metallocene catalysts, constrained geometry complexes (CGC), and post-metallocene complexes have low compatibility with polar functional groups, such as Brønsted acids and heteroatom-containing functionalities. In particular, polar vinyl monomers are hardly used for early transition-metal catalyzed co-polymerization with non-polar olefins. Since polar vinyl monomers such as acrylates, vinyl ethers, vinyl fluoride, acrylonitrile, and vinyl acetate are commercially important, it is one of the most significant challenges in polymer chemistry to achieve random incorporation of polar vinyl monomers with precise control of polar/non-polar ratios and polymer microstructures [21]. The discrete manipulation of late transition metal catalysts makes it possible to directly co-polymerize polar monomers with non-polar olefins by reducing their oxophilicity and tolerance to other functionalities. Recently, ring-opening metathesis polymerization of functionalized cyclooctenes, acyclic diene metathesis polymerization of symmetrically substituted α,ω-dienes, other controlled polymerization techniques have also been developed for producing the functionalized linear polyolefins. Here, the discussions are limited to olefin polymerizations that proceed via the coordination–insertion mechanism in order to further distinguish from free radical, controlled free radical and other types of metal-mediated polymerizations that are facilitated by organometallic complexes.

3. Single-site N-heterocyclic organometallic catalysts containing a five-membered ring system

Non-metallocene organometallic catalysts composed of N-donor heterocyclic ligands bearing monometallic centers have long been at the forefront of catalytic research and are studied extensively for olefin oligo/polymerization. Many academic and industrial researchers have surveyed the use of these catalysts as polymerizing agents with desired compositions. In particular, much attention has been paid to the polymerization of ethylene, propylene, and norbornene into polyethylene, polypropylene, and polynorbornene, respectively. Increasing effort is now being made in exploring the structure–reactivity relationships in N-donor heterocyclic ligand systems as they can form "constant geometry" complexes with alkyl/aryl/aralkyl/alkylsilyl metal precursors. This particular section focuses on exploring the coordination chemistry of ligands with potential N-donor heterocyclic compounds to form mononuclear organometallic catalysts with different heterocyclic rings and investigating the catalytic properties of these catalysts in olefin oligo/polymerization. The preparation, structure, and a olefin oligo/polymerization products of mononuclear organometallic N-heterocyclic catalysts are presented in the three following sub-sections, each limited to N-heterocyclic ring systems with a specific number of ring members for convenience.

A vast number of catalysts bearing five-membered heterocyclic ring systems are efficient for olefin trimerization, oligomerization, and polymerization. In particular, N-heterocyclic organometallic catalysts are effective compounds, especially in the oligo/polymerization of ethylene, propylene, and norbornene. This class of catalysts is composed of two kinds of N-heterocyclic systems, namely, polypyrazoles, pyrrole, and imidazole derivatives.

3.1. Pyrazole-based catalysts

There are few pyrazole-based monometallic organometallic compounds with the title activities. The main class of these catalysts is derived from tripyrazolyl-borate derivatives, also known as poly(pyrazolyl) borates, which serve as tridentate, tripodal ligands with three N-donors from three pyrazole rings connected to a boron atom with another set of nitrogen atoms on another side. The growth of this class of ligands and the catalysts derived has been accelerated for many years; however, none of it was mentioned in the most recent reviews, which are devoted only in part to coordination-controlling ligands and their chemistry.

Early transition half-sandwich compounds generally have low activity in olefin oligo/polymerization. This has motivated many studies into non-metallocene compounds containing ligands with properties similar to that of the cyclopentadienyl (Cp) group. From this perspective, pyrazole derivatives are similar to the Cp group in terms of the count of pi-electrons and planarity, which has grabbed the attention of many researchers. Representative active catalysts derived from pyrazole scaffolds are shown in Fig. 1. Monoanion was prepared through the disarticulation of 1,2-bis(dimethylphosphino)ethane $Me_2PCH_2CH_2PMe_2$ (dmpe) by tripyrazolyl borate (Tp) from $Ti(CO)_5$(dmpe) and was isolated as a tetraethyleamino salt. This derivative is remarkably stable against air oxidation and represents the first example of N-coordinated zerovalent titanium [22]. Furthermore, titanium complexes with the compositions $TpTi(OR)Cl_2$, $TpTi(OR)_2Cl$, and $TpTi(OR)_3$ were synthesized and used to obtain alkyltitanium compounds suitable for olefin polymerization of structures $TpTi(OR)Me_2$, $TpTi(OR)_2Me$, and $TpTi(OR)CH_2SiMe_3$ (**1**), through a reaction using the appropriate Grignard reagents. These Tp-coordinated alkyl-titanium catalysts act as efficient ethylene polymerization catalysts with selectivity and reactivity. Nomura et al. [23] reported something interesting about a titanium complex cation $[TpTiMe(2,6\text{-}MeC_6H_3O)]$ that rules out conventional ethylene polymerization. The titanium complex cation readily polymerizes ethylene into linear polyethylene without any assistance from alkyl aluminum co-catalysts. The presence of the fluroboron anion and the methyl attachment to the catalyst are the basic concepts for the catalyst design. Many catalysts for the polymerization of ethylene were prepared based on the reaction of Tp as well as for methyl polypyrazolylborates with alkyl or aryl Ti compounds and aluminum alkyls. These catalysts behave distinctly according to the influence of substitutions with Tp and the organic part attached to the metal ions.

A cationic complex $[Me_2TpZr(CH_2Ph)_2]$ is generated quantitatively by the reaction of $[Me_2TpZr(CH_2Ph)_3]$ with $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at $-60\,^\circ C$. This cation is generated at low temperature and rearranges rapidly at $0\,^\circ C$ to the bis-(pyrazolyl)borate complex **2**. Both cation and **2** are highly reactive for ethylene and alkyne insertions. The reactions of both the compounds with 2-butyne were explored to compare the insertion reactivity of these species, which further forms methylstyrenes instead of polymers. Catalyst **2** undergoes three successive 2-butyne insertions followed by intramolecular insertion/cyclization yields in the intermediate stage before finally ending with the elimination of cyclopentadiene instead of forming a polymer [24]. Similar rearrangements can be anticipated for other group IV metals [25].

Numerous attempts have been made in Tp and alkyl-substituted Tp coordination with group V alkyl or aryl metal precursors to obtain exceptionally good activity in olefin polymerization in the hope that the group V catalysts would be more tolerant to functionalized monomers, which is a highly desirable property if co-polymers are targeted. Vanadium complexes have frequently been used as catalysts but are readily reduced to lower oxidation states upon the addition of a co-catalyst. However, vanadium(V) complexes would also be effective olefin polymerization catalysts if they could be stabilized in their high oxidation state. With Tp or related compounds, the reactivity of vanadium catalysts is almost negligible; however, niobium catalysts have been reported to be efficient catalysts. Many observations have been made when alkyl niobium complexes such as $[TpNbMe_2(PhC{\equiv}CMe)]$, $[TpNb(Cl)(CH_2SiMe_3)(PhC{\equiv}CMe)]$ (**3**), $[TpNb(Cl)(CH_2Me)(PhC{\equiv}CMe)]$ (**4**), and $[TpNb(Cl)(Me)(PhC{\equiv}CCH_2SiMe_3)]$ subjected to ethylene polymerization are activated by the methyl abstracting agent $B(C_6F_5)_3$ in toluene. The activities are higher than those observed for previously described systems based on the heavier group V organometallic complexes. The choice of the aluminum-based activator is critical in group V systems. Furthermore, the activity is notably dependent on the nature of Tp. Bulky 3,5-dimethyl and 3,5-dimethyl-4-chloro substituted Tp leads to a much higher catalytic activity than the less sterically demanding unsubstituted Tp. These effects may be the result of steric shielding of the niobium center by substituted Tp, which then prevents decomposition of the catalytic species through association to afford inactive dinuclear species that terminate further polymerization. Furthermore, rare examples of alkyl cations of niobium directly related to the active species in ethylene polymerization have been found with the catalyst possessing a

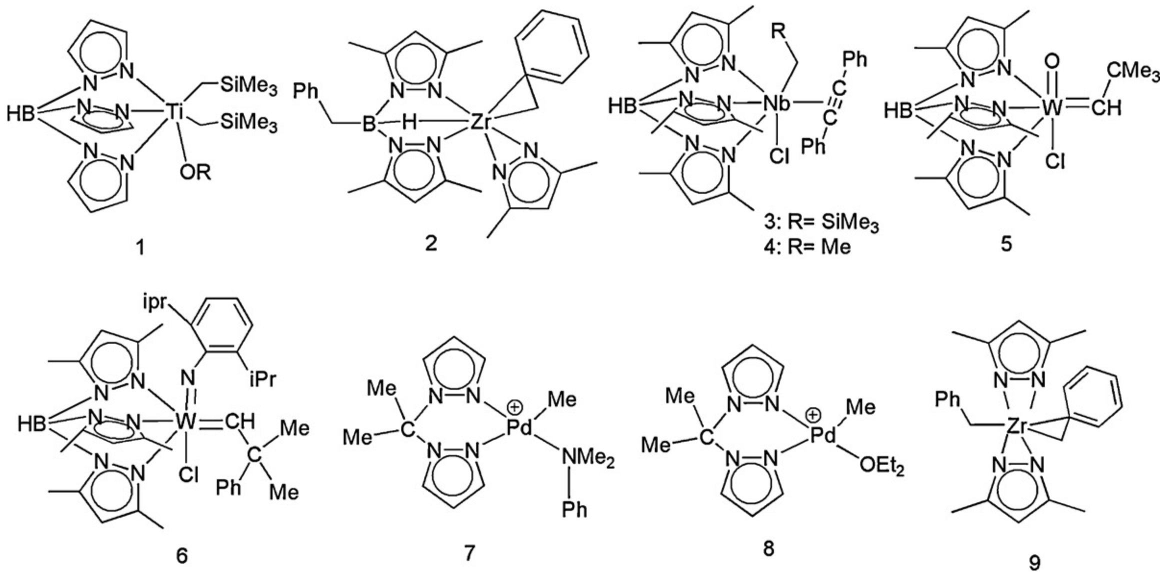


Fig. 1. Pyrazole-derived non-metallocene organometallic catalysts.

dialkyl/aryl phosphene base. Stabilization is effected by the unique electronic and steric properties of dimethyl-substituted Tp and the 4e alkyne ligands in tandem with the non-coordinating properties of the Brookhart anion (BArf$_4$) Arf: 3,5-$C_6H_3(CF_3)_2$ [26].

In general, the olefin polymerization of group VI non-metallocene organometallic compounds with Tp, especially with tungsten system, have also been studied to the same extent as those for group IV and V metals. [TpW(=C(H)Bu^t)(0)Cl] (**5**) was prepared by the reduction of the highly stable [TpW(=CBu^t)Cl$_2$] complex, and the structure of which was determined by X-ray crystallographic methods is effective for catalyst olefin polymerization. Complex **5** in combination with one equivalent of $AlCl_3$ catalyzes ring-opening polymerization of cyclooctene or norbornene readily to a high polymer even in the presence of air. A five-coordinate cationic alkylidene has also been estimated to be the active catalytic species formed during the polymerization process [27]. Not only oxo-tungsten alkene catalysts are active in polymerization; a series of imino non oxo-tungsten alkene catalysts were also prepared and tested for olefin polymerization properties. Catalyst **6** and its derivatives were inert towards cyclooctene when alone, but they caused rapid ring-opening polymerization with remarkably good activity in the presence of aluminum salt like $AlCl_3$ [28].

Tp reacts with group VII and VIII metals to form stable organometallic compounds, which were prepared according to the method employed for the preparation of earlier catalysts. However, many of these catalysts were studied as catalysts for olefin hydrogenation, not as polymerization catalysts. These catalysts, especially ruthenium catalysts, are active with turnover numbers up to 200; methyl acrylate is hydrogenated to methyl propionate, while allylbenzene is partly hydrogenated to propylbenzene [29] instead of the formation of polymethyl acrylates or polyallybenzenes. Furthermore, Tp with group IX metals, especially rhodium complexes, showed interesting activity in C–H bond activation [30]. Later transition organometallic catalysts with Tp were not studied to the earlier extent due to their lesser/no activity towards olefin polymerization.

Apart from tripyrazolyl borates, bis(pyrazolyl)methane ligands are also efficient at producing methyl palladium catalysts for ethylene oligomerization. Cationic Pd(II) alkyl complexes containing a neutral bidentate nitrogen donor ligand like the Bis-pyrazolyl derivative and a labile ligand or substrate cis to the alkyl group undergo a variety of important insertion reactions and are active species for olefin polymerization, olefin/CO co-polymerization, and olefin/alkyl-acrylate co-polymerization [31,32]. The reaction of (COD)PdMeCl with the appropriate bis(pyrazoyl)methane like $Me_2C(Pz)_2$, $Ph_2C(Pz)_2$ Pz: pyrazole in methylene chloride yields [{$Me_2C(Pz)$}PdMeCl], [{$Ph_2C(Pz)$}PdMeCl], which upon treatment with N,N-dimethylaniline[$B(C_6F_5)_4$] or [$H(OEt_2)_2$][B{3,5-$(CF_3)_2C_6H_3$}$_4$] yields complex cations **7** and **8** by aniline or ethoxy insertion reactions, respectively, in a process called protonolysis [33–35]. Furthermore, Cation **7** undergoes ligand substitution reaction in the presence of ethylene to form a methyl ethylene palladium cation which oligomerizes ethylene to C_8–C_{24} internal olefins. The detailed mechanism of the formation of higher oligomers is shown in Fig. 2. The efficiency of ethylene oligomerization by the ethylene palladium cation appears to be limited by catalyst stability. These catalysts are very selective for the insertion of ethylene versus α-olefins, and β-hydride elimination is competitive with olefin insertion; this produces high-quality linear α-olefins from ethylene. Bis(pyrazolyl)methanes support insertion chemistry at cationic Pd(II) alkyl centers, but modification to increase the binding constants of these ligands will be required to obtain more robust catalysts in olefin oligo/polymerization in general. A key advance in this area was the recognition that chain transfer in olefin polymerization by these systems proceeds by associative olefin replacement and that the use of bulky bidentate bis-pyrazolyl ligands that block the apical coordination sites hinders this process [36,37].

In contrast, a very different coordination mode of 1H pyrazole [23] was observed in many cases, i.e., both the hetero nitrogen atoms chelate to a single metal atom/ion. For instance, mononucleating 3,5-dimethyl pyrazole readily reacts with [$Zr(CH_2Ph)_4$] at a 2:1 molar ratio to yield a dibenzyl complex [Zr(3,5-$Me_2Pz)_2(CH_2Ph)_2$] **9** through an alkane elimination reaction in which both the nitrogen atoms of the pyrazole ring are coordinated to zirconium [38]. The zirconium complex **9** has been preliminary examined as a catalyst precursor for ethylene and propylene polymerization upon activation with MAO. No polymerization of propylene using **9** occurred at any operating temperature or olefin pressure. This lack of activity has been attributed to the non-generation of catalytically active species in the solution, probably resulting from the premature decomposition of the dimethyl zirconium intermediate when the dialkylation occurred from MAO. Polyethylene was exclusively isolated using **9**; at 1 atm ethylene

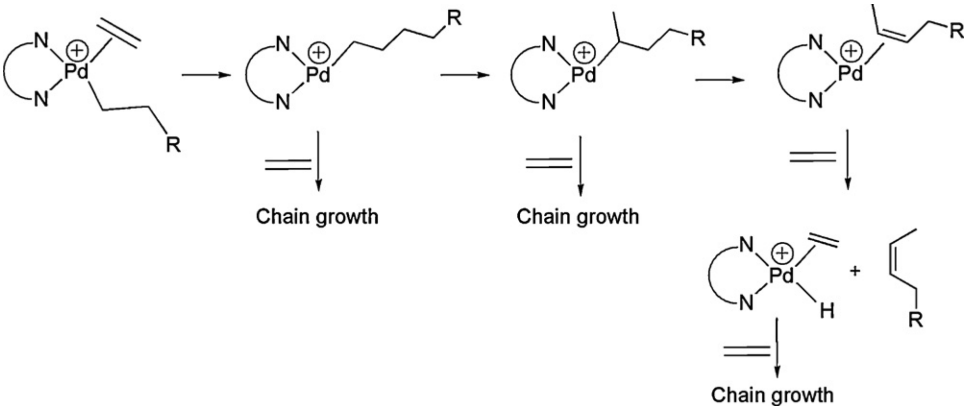


Fig. 2. Mechanism of ethylene oligomerization by pyrazole-derived palladium catalysts.

pressure, low activity was observed before 30 min independent of temperature. Activity increased with time from 30 min but was ca. twofold greater at 60 min than 30 min regardless of temperature. In contrast, at 4 atm and 25 or 50 °C, the catalytic activity of **9** depends on the polymerization time. At 50 °C, the highest activity occurs at up to 5 min followed by a rate decrease to a roughly constant value of 4 kg polymer/(mol Zr h atm ethylene).

3.2. Pyrrole-based catalysts

Pyrrole is another class of N-heterocyclic compound characterized by a five-membered ring with four sp^2 hybridized carbon atoms and a nitrogen heteroatom. Recently, 2- and 2,5-disubstituted pyrroles have gained attention as many of their organometallic catalysts are efficient olefin polymerization catalysts. Pyrrole-based ligands ensure the preparation of polyethylene with a very high molecular weight. The great amount of patented work found in this research field may be due to the high catalytic activity if pyrrole-based ligands towards olefin oligo/polymerization.

Mono or bis-imine pyrrole-based ligands with substitutions at 2- and/or 2,5- positions have the potential to form chelate rings of varying sizes. Chelating diimines with substituents at 2- and/or 2,5- are readily accessible by reaction with alkyl metal salts to form complexes with a greater ability for oligo/polymerization of olefins. These mono or bis-imine pyrrole-based ligands can be formed by a simple imine reaction with 2-formyl pyrrole having alkyl mono or diamines, respectively. Also, 2,5-diformyl/acetyl pyrrole reacts with alkyl/aryl amines to form tridentate NNN donor ligands suitable for olefin polymerization. Apart from these imine bi, tri or tetra-dentate ligands, many substituted pyrroles such as pyrrole-2-carboxylic acid, pyrrole-2,5-dicarboxylic acid, and pyrrole-3-carboxylic acid are also used as the ligands of choice for the said purpose. These ligands are flexible; the range of possible coordination modes includes five- and six-membered rings depending on the precursors used with different metal atom/ions. The wide range of metal-to-nitrogen (amido/imine) distances in such complexes underlines the ability of amido/imine ligands to act as one to three lone-pair electron donor ligands, including deprotonation from the pyrrole ring proton. With polydentate ligands, a meridional geometry of the heteroatom donors and transoid arrangement of the alky/aryl/aralkyl ligands is favored, i.e., a geometry that does not favor alkene insertion and chain growth by the accepted Ziegler mechanism [39,40]. Representative active catalysts derived from pyrrole scaffolds are shown in Fig. 3.

Pyrrolide-imine (PI compounds) (both mono and bis-imines) compounds are efficient ligand systems for preparing group IV organometallic catalysts for olefin polymerization. Bis(pyrrolide-imine) titanium complexes are of great interest in the commercial production of polyolefin. Aside from the bis(pyrrolide-imine) titanium complexes, many zirconium and hafnium counterparts (Zr- and Hf-PI catalysts) are also useful in the preparation of polyolefin, particularly polyethylene; they have proved to be highly active catalysts for the polymerization of ethylene. Thermally robust dibenzyl hafnium and zirconium complexes with two pyrrolide-imine ligands are accessible by the proper choice of the imine substituent. Dibenzyl hafnium complexes can be converted into benzyl cations by the reaction of $B(C_6F_5)_3$, which polymerizes ethylene with very high activity. Catalyst **10**, which bears a 1-adamentyl group on the imine-N, demonstrates a high activity of 22,900 kg-PE/mol-cat/h in association with MAO [41]. In addition, the hafnium congener **11** polymerizes ethylene with an activity of 2100 kg-PE/mol-cat/h under the same conditions. These results show that in addition to Ti-PI catalysts, Zr- and Hf-PI catalysts are also useful catalysts for ethylene polymerization, which in turn indicates the high potential of pyrrolide-imine ligands for olefin polymerization [42].

Ziegler et al. [43] studied the molecular mechanics of single-site ethylene polymerization catalyzed by titanium or zirconium catalysts derived from pyrrole-2-imine ligand in the presence of a boron-based counterion using DFT calculations. The ligand was prepared as a product between the condensation of pyrrole-2-carboxaldehyde and aniline. Both complexes are octahedral in nature with one imine and one chloride at the axial positions. Calculations were carried out to investigate the insertion of the ethylene monomer into the M-methyl (M: Ti or Zr) bond after activation with alkyl aluminum compounds for pyrrole-2-imine systems. Furthermore, second insertion studies have also been conducted for catalysts stabilized by boron counterions. According to the study, for the titanium-based system, the uptake of ethylene determines the rate for the *cis* approach with the total barrier being 12.9 kcal/mol, and the insertion barrier determines the rate for the *trans* approach with the total barrier being 13.8 kcal/mol. For the zirconium-based system, the insertion barrier determined the rates for both the cis and trans approaches with the total barriers being 9.4 and 10.6 kcal/mol, respectively (Fig. 4).

A series of amido pyrrolyl complexes of zirconium and hafnium were prepared by the reaction of tetrabenzyl-zirconium and -hafnium with 2,5-bis(*N*-aryliminomethyl)pyrrole dianionic tridentate ligands, respectively, by Mashima et al. [44]. The zirconium complexes **12** and **13** bearing bulky substituents at the nitrogen atoms of the ligand exhibited high catalytic activities (**12**, 131 (kg PE)(mol cat)$^{-1}$ h^{-1} at 60 °C; **13**, 458 (kg PE)(mol cat)$^{-1}$ h^{-1} at 75 °C) upon combining with 1000 equiv of MMAO. Lewis base–free cationic alkyl complexes **16**–**19** were prepared by alkyl abstraction from the corresponding dibenzyl complexes of zirconium **12**,

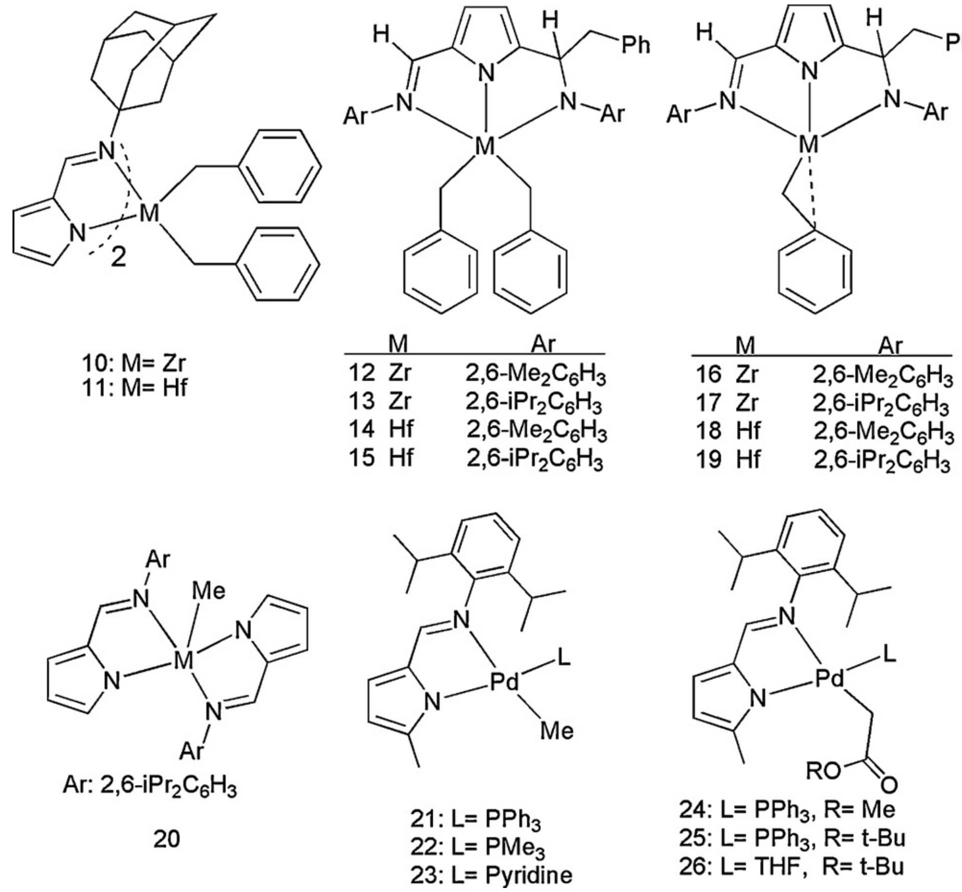


Fig. 3. Pyrrole-derived non-metallocene organometallic catalysts.

13 and hafnium **14**, **15**; the resulting cationic complexes **17** and **19** catalyzed ethylene polymerization without MMAO. At elevated temperatures, the few complexes behaved in an interesting manner and produced good activity compared to at room temperature. For complex **13**, the highest polymerization activity was obtained at 75 °C, where the activity was 10 times higher than at room temperature, indicating that at the latter the insertion of ethylene into the metal–carbon bond of catalytically active cationic species is prevented to some extent by steric bulkiness of the imino and amido moieties. Similarly, complex **12** showed the highest activity of polymerization at 60 °C. The polyethylenes obtained by using **12** and **13** at various temperatures have rather broad M_w/M_n values (26.7–51.4 for **12**; 17.5–43.2 for **13**), due to the thermal instability of the catalytically active species under the polymerization condition. Overall, most of the benzyl-substituted zirconium complexes were concluded to be superior in activity to the corresponding hafnium complexes.

A brick-red colored catalyst is readily prepared by the action of $Zr(CH_2Ph)_4$ on diimine in freshly distilled toluene [45]. The diimine ligand was prepared by treating pyrrole-2-carboxaldehyde with ethylene diamine in ethanol at lower pH conditions. However, the polyethylene produced with the imine complex was in most cases of unusually high molecular weight; this is indicative of the formation of catalytically highly active centers, even if in low concentrations.

A comprehensive approach was made by Lashier and Bartlesville [46] in their European patent disclosing many facts about chromium organometallic pyrrole derivatives as olefin oligomerization catalysts. A novel process trimerized or oligomerized olefins in the presence of said catalysts and a solvent that is a product of the olefin oligomerization process. These catalysts are mainly comprised of an alkyl chromium precursor, pyrrole-based ligands, and a metal alkyl compound. Furthermore, Freeman et al. [47] claimed very interesting things in their patent about pyrrole-based alkyl/aralkyl chromium catalysts as olefin polymerization agents. Prepared catalyst systems are useful and comprised of an alkyl/aralkyl chromium source, pyrrole-containing compound, and metal alkyl, all of which react in the presence of an unsaturated hydrocarbon. Such catalyst systems are especially useful for the oligomerization of olefins such as ethylene, propylene, and 1-hexene. The chromium source, wherein the chromium oxidation state ranges from 0 to 6, is preferably a chromium(II) and/or chromium(III)-containing compound that can yield a catalyst system with improved oligo/trimerization activity; these are used extensively because of the ease of use, availability, and enhanced activity. Specific examples of chromium(III) compounds include chromium(III)-2,2,6,6-tetramethylheptanedionate [$Cr(TMHD)_3$], chromium(III)-2-ethylhexanoate [$Cr(EH)_3$], etc. Examples of pyrrole-containing compounds used to get olefin trimerization catalysts include hydrogen pyrrolide (1H-pyrrole), lithium pyrrolide, sodium pyrrolide, potassium pyrrolide, cesium pyrrolide, and/or the salts of unsubstituted pyrrolides; these compounds have high reactivity with the other reagents. The substituted pyrroles used are pyrrole-2-carboxilic acid, 2-acetylpyrrole, pyrrole-3-carboxaldehyde, 2,5-dimethylpyrrole, 2,4-dimethyl-3-ethylpyrrole, 3-acetyl-2,4-dimethylpyrrole, ethyl-2,4-dimethyl-5-(ethoxycarbonyl)-3-pyrrole-propionate, ethyl-3,5-dimethyl-2-pyrrolecarboxylate, and mixtures thereof (Fig. 5).

All of these pyrrole-containing catalysts can produce a catalyst system with high activity and productivity; however, the use of pyrrole and 2,5-dimethylpyrrole can produce a catalyst system with

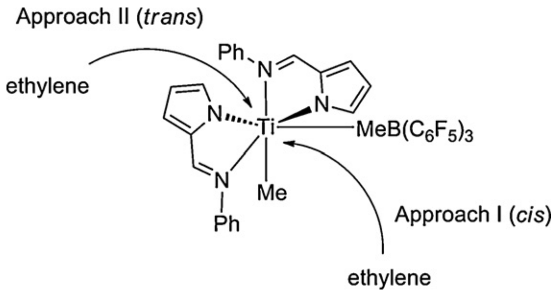


Fig. 4. Different modes of approach for the ethylene monomer towards the active species of 2-imine pyrrole-derived catalysts.

enhanced activity and selectivity to a desired product. More importantly, the metal alkyl can be any heteroleptic or homoleptic metal alkyl compound; even one or more metal alkyls can be used to get alkyl chromium derivatives as active species in the oligomerization process. A few examples of the metal alkyls used for the study are alkylboron compounds, alkylmagnesium compounds, and alkyllithium compounds.

The imino-pyrrolide Cr(III) complex **20** was reported by Gibson et al. [48] to be an efficient ethylene polymerization catalyst. The catalyst was prepared by the action of pyrrole-2-carboxaldehyde on 2,6-diisopropyl aniline at −78 °C in tetrahydrofuran with *n*-butyl lithium for an abstracting pyrrole ring proton and helps coordination via deprotonation. The catalyst **20** affords an ethylene polymerization activity of 70 g mmol^{-1} h^{-1} bar^{-1} in combination with Et$_2$AlCl. Slightly lower activities have been reported for the binuclear Cr(III) complex of the analogue derived from non-heterocyclic N-donor ligand systems and for the related binuclear Cr(III) complex bearing less bulky phenyl substituents.

Several additional classes of ethylene polymerization catalysts based upon tridentate ligand complexes of iron have been developed and patented. These include the pyrrole-2,5-diimines formed as condensation products of pyrrole-2,5-dicarboxaldehyde and 2,6-, 2,4,6- substituted anilines. The oxidation state of the metal in these pyrrole derivatives is not clear from the claims.

Most importantly, nickel and palladium complexes of mono and diimine ligands with 2,4-substituted anilines are capable of producing polymers with different olefins and co-polymers with various functionalized vinyl comonomers such as methyl acrylate, methyl methacrylate, and functionalized cyclic olefins. Neutral alkyl pelladium catalysts with pyrrole imines have also attracted considerable attention because of their special characteristics resulting from the reduced charge at the catalytic center. Dramatic differences have been observed between neutral and cationic nickel catalysts. Although both species can display high activities in ethylene polymerization, the neutral catalysts show considerably more tolerance towards polar groups. This has allowed the extension of their use to the co-polymerization of ethylene with a wider range of α,ω-functionalized olefin monomers. Novak et al. [49] have reported three novel (**21**, **22** and **23**) methyl palladium catalysts for methyl acrylate polymerization. The polymers produced have high molecular weights (M_n > 138,000) and show glass transition temperatures of 10.4 °C. According to NMR spectral studies, the atactic polymers were obtained in all cases, as were the poly(methyl methacrylate) samples prepared. Likewise, methyl acrelate and olefins have been successfully co-polymerized, and the co-polymers produced are generally acrylate-rich. Collectively, all of these mechanistic studies support a radical mechanism for methyl acrelate polymerization using neutral palladium complexes. The radical formation is believed to occur because of the hemolytic cleavage of the Pd–Me bond; thus, neutral methyl palladium(II) complexes appear prone to trace radical reactions that can effectively initiate the polymerization of reactive monomers like α-olefins, acrelates, etc.

The nature of the metal–carbon bond and substituents attached to the carbon atom plays a crucial role in the olefin polymerization. For instance, catalysts **24**–**26** are prepared from the same ligand from which **21**–**23** are derived. These catalysts differ only at one site—that is, methyl is replaced by enolate—and the neutral palladium enolates are very stable at temperatures of up to 50 °C. However, all attempts at methyl acrylate polymerization were performed using these neutral palladium enolates as initiators; surprisingly, none of them showed activity, which may be because of the bulkier enolate fraction.

3.3. Imidazole/oxazole/thiazole-based catalysts

These heterocyclic systems have two heteroatoms at positions 1 and 3 positions; that is, nitrogen and nitrogen or oxygen or sulfur atoms give imidazole, oxazole, and thiazole, respectively. These heterocycles are planar in nature and characterized with three sp^2 hybridized carbon atoms at positions 2, 4, and 5 and heteroatoms at positions 1 and 3. The catalysts formed by 2-substituted derivatives of these heterocycles usually have heterocyclic nitrogen donors (imine nitrogen); however, another heteroatom (nitrogen or oxygen or sulfur) is present outside the coordination sphere to form more stable coordination catalysts. Representative active catalysts derived from imidazole, thiazole, and oxazole scaffolds are shown in Fig. 6.

Comprehensive studies on imidazole-derived catalysts with group III–XI metal ions having direct metal-to-carbon bonding have been patented by Gibson et al. [49,50]. The purpose of their discovery is to provide catalysts for oligo/polymerizing monomers such as olefins, cycloolefins, or diolefins, especially ethylene and propylene, or for co-polymerizing ethylene with higher 1-olefins with high catalytic activity. The catalysts developed by Gibson et al. show extremely high activity for the oligo/polymerization of olefins, which leads to many benefits, including lower catalyst loadings in commercial processes and lower catalyst residues in the final product. The catalysts are comprised of the transition metal compound with formula **27** and a suitable activator such as organoaluminum or organoboron compounds or mixtures thereof. Compounds with the general formula **27**, where Z is comprised of a five-membered heterocyclic ring (viz., imidazole, thiazole, or oxazole), M is a group III–XI metal, E1 and E2 are divalent groups (aliphatic, alicyclic, aromatic, etc.), D1 and D2 are donor atoms, X is an anionic group, and L is a neutral donor group.

The metal is preferably from groups III to VII (viz., Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and Mn) in the form of the methyl, benzyl, or phenyl carboxylate, or an oxide, alkoxide, or hydroxyl salt. Gibson et al. selected an imidazole core as Z for more efficient catalysts with different substituents (Fig. 7a). R1–R7 are independent hydrogen or monovalent aliphatic hydrocarbons (viz., methyl,

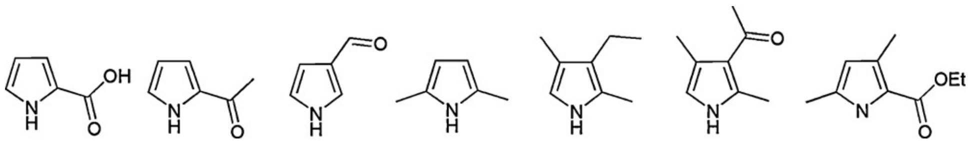


Fig. 5. Substituted 1H-pyrrole derivatives as ligands in the preparation of non-metallocene organometallic catalysts.

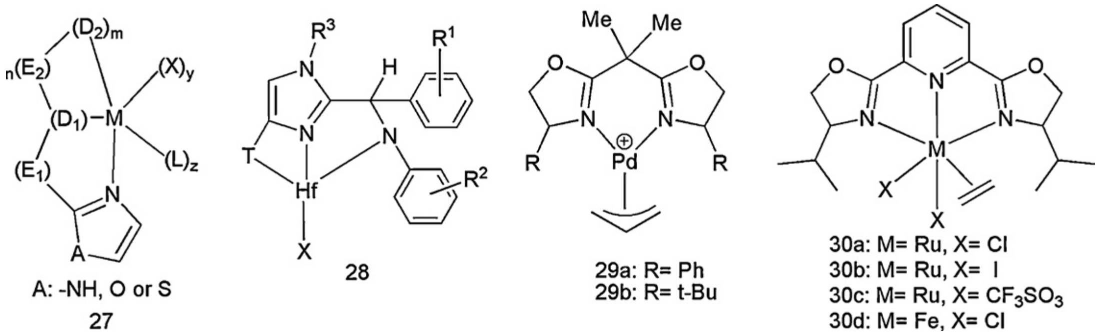


Fig. 6. Imidazole, thiazole, and oxazole scaffolds based on non-metallocene organometallic catalysts.

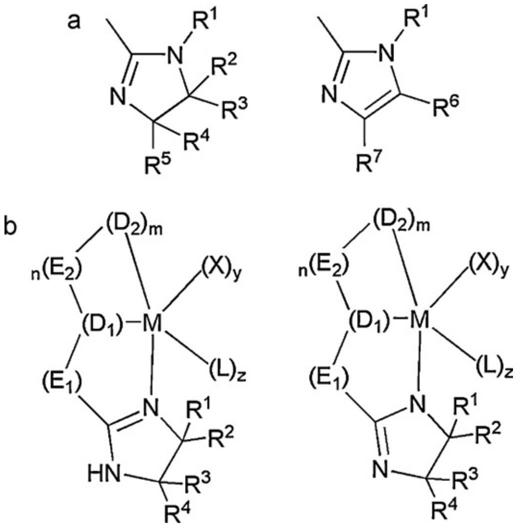


Fig. 7. Substituted imidazole derivatives (**7a**) and their mode of involvement in the coordination to form active catalysts (**7b**).

ethyl, ethylenyl, butyl, hexyl, isopropyl, and turt-butyl), alicyclic hydrocarbons (viz., adamantyl, norbornyl, cyclopentyl and cyclohexyl), aromatic hydrocarbons (viz., phenyl, naphthyl, biphenyl, phenanthryl, and anthranyl), alkyl-substituted aromatic hydrocarbons (viz., benzyl, tolyl, mesityl, etc.), or heterocyclic groups or their derivatives. The modes of coordination of the imidazole ring in the complex formation are shown in Fig. 7b. These alkyl metal catalysts are employed in the co-polymerization of 1-olefins wherein the monomer is selected from ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, octane, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, vinyl chloride, and styrene. Finally, the polymers formed are of great interest in molecular weight distribution and stiffness. These studies predict that the morphology of the formed polymers depends on the architecture of the imidazole-derived catalyst in which the mode of coordination of the ring nitrogen atoms plays a significant role.

Articles in the literature [51,52] have reported ortho-metallated hafnium complexes of imidazole derivatives as catalysts **28**. The 4-position of imidazole consists of a cycloaliphatic or aromatic group containing one or more rings through which any one of the carbon atoms make a stable sigma bond with the hafnium ion. The fourth coordinating site (X) is preferably covered by the C_{1-20} hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl groups. The 2-carbazolyl (R^3) substitution on the imidazole ring still increases the activity of the catalyst formed and produces more desirable products. These catalysts are highly efficient, especially in the olefin polymerization process, where one more additional polymerizable monomer is polymerized in the presence of hafnium catalysts **28**, including preferred embodiments, to form a high molecular weight tactic polymer—this is isotactic or highly isotactic—with improved operating efficiency. These processes can operate at high catalyst efficiencies to prepare polymers with desirable physical properties.

In addition, many imidazole-derived catalysts preferably form N-heterocyclic carbenes (NHCs) in which coordination usually occurs through the carbene rather than ring nitrogen to form stable organometallic compounds [53]. However, few benzo-fused imidazole catalysts act as N-heterocyclic donors for the formation of non-metallocene transition metal catalysts for olefin oligo/polymerization. NHCs act as versatile compounds depending upon the substituents in the imidazole ring. 1,3-Diisopropylimidazole derivatives act as NHC towards allyl ruthenium salt to form allyl organo-ruthenium compounds suitable for ring closing metathesis leading to tetra-substituted olefins [54]. In contrast, transition metal derivatives of borane or alumane imidazolinides such as bis(tris(pentafluorophenyl)borane)imidazolinide and bis(tris(pentafluorophenyl) alumane)imidazolinide act as ethylene and propylene polymerization agents in slurry and gas phases, wherein the polymer product formed has a bulk density greater than 0.3 g/ml [55].

Oxazole and thiazole-bearing organometallic catalysts employed in olefin polymerization display excellent abilities and have similar properties to those of imidazole-substituted catalysts. Rare examples are available for these class of catalysts in terms of olefin oligo/polymerization. Early transition metal derivatives with aliphatic and aromatic substituents having oxazole or thiazole rings were studied by Gibson et al. for their patent [50], which mainly describes the formation of high molecular weight polymers from ethylene and propylene co/polymerization.

Two chiral Pd(II) allyl catalysts **29** and **30** derived from a dioxazolidine derivative were efficient polymerization catalysts producing addition polymers with molecular weights above 10,000 and composed of triangular repeating units starting from 3,3-dialkylcyclopropenes as the monomer [56]. A relatively moderate degree of tacticity was observed in the addition polymers, indicating that both catalytic site and chain-end controls contribute to the overall stereo control in the polymerization of 3,3-dimethylcyclopropene catalyzed by **29(a)**. However, the explanation about the polymers formed by **29(b)** is not clear. Similarly, for (bisoxazoline)Pd(II)-catalyzed alternating co-polymerization of *p-tert*-butylstyrene and CO, the chain-end control mechanism can be overridden due to the higher flexibility of the growing polymer chain [57]. This can be concluded as the steric bulk of the chelating ligand of the Pd catalyst, and the size of the monomer substituents affect the polymerization behavior of the cyclopropene derivatives, which in turn affects the properties of the polymers formed thereafter.

The series of group VIII complexes **30(a)**–**(d)** were effective catalysts for ethylene and 1-hexene polymerization with the bis-oxazoline ligand system through an isopropyl substitution [58,59].

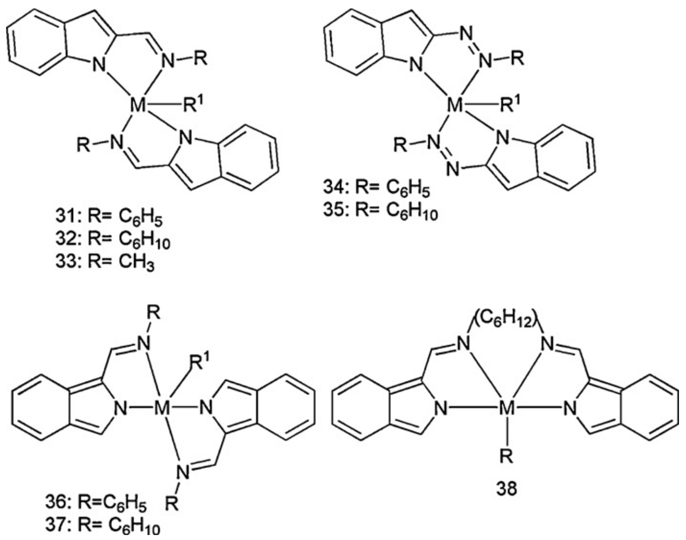


Fig. 8. Catalysts derived from benzo-fused five-membered heterocyclic scaffolds involved in olefin polymerization.

A large number of 2,6-bis(2-oxazoline)pyridine ligand systems (also called pybox ligands) employed in the preparation of active catalysts for olefin polymerization are available in the literature; however, very few reports were found on the organometallic non-metallocene catalysts desired for the said activity. The iron(II) and ruthenium(II) catalysts of the ligand system 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine] in combination with the MAO co-catalyst exhibit moderate catalytic activity for both ethylene homopolymerization and ethylene/1-hexene co-polymerization. Only a linear polyethylene is obtained if an iron catalyst is employed under the same co-polymerization conditions. Notably, the ruthenium catalysts **30(a)**–**(c)** show good catalytic activity for ethylene/1-hexene co-polymerization with good yield.

Few iridium allyl catalysts with thiazole backbone have been studied for the stereochemical outcome of iridium-catalyzed olefin hydrogenation processes with excellent yields rather than polymerization [60]. Apart from these, there are many other important oxazole and thiazole-derived ligand systems with suitable transition metal ions reported for olefin polymerization; however, they have very few organometallic complexes that have been reported. Similar to imidazole derivatives, these azole derivatives can also form NHCs and show ring opening and closing metathesis. Ruthenium-based complexes with a thiazole backbone are adequate catalysts for ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization. In particular, the phosphine-free thiazole-2-ylidene bearing catalysts are unexpectedly robust; they show stability and activity comparable to those of existing NHC-containing ruthenium catalysts, for example, ring closing of diethyldiallyl malonate even at 60 °C [61].

3.4. Benzo-fused five-membered N-heterocyclic catalysts

An important class of benzo-fused five-membered N-heterocyclic compounds is comprised of indole, isoindole, benzimidazole, benzoxazole, and benzothiazole. Despite massive efforts in industrial and academic research laboratories to ascertain new olefin polymerization catalysts, no major breakthrough has yet been achieved using benzo-fused non-metallocene organometallic N-donor heterocyclic transition metal catalysts. The catalysts derived from benzo-fused five-membered heterocyclic scaffolds are shown in Fig. 8. Some recent research outcomes describe the ethylene and propylene oligo/polymerization activity of complexes derived from said ligand systems (not all), in which metal is directly attached by alkyl or aryl carbon atoms. Shigekazu et al. reported in their patent [62] that few N-donor indole and isoindole ligands in combination with alkyl or aryl transition metal compounds act as olefin (co)polymerization catalysts with good activities; they also claimed a process for olefin polymerization using these as efficient catalysts. Catalysts **31**–**38** are specified olefins; in particular, ethylene polymerization catalysts consist of indole or isoindole N-donor ligand systems with group III–IX transition metal ions having an alkyl group directly attached to the metal center. All catalysts can produce polymers of the desired compositions and are efficient polymerization catalysts in the presence of an alkyl aluminum activator. The transition metal ions used in the study were Sc(III), Ti(III), Ti(IV), Zr(III), Zr(IV), Hf(IV), V(IV), Nb(V), Ta(V), Co(II), Co(III), Rh(II), Rh(III), and Rh(IV). Finally, Ti(IV), Zr(IV), and Hf(IV) catalysts were concluded to show the best activity of the series. In all of these cases, X is a methyl group and may be two or more depending upon the valence of the metal ions. Apart from these, halogen-substituted—preferably fluorine—indole derivatives possess a different activity as catalyst activators for olefin polymerization. In a recent patent, the activators of the invention include an indole component and alkyl aluminum or aluminoxane. The activator is a reaction product of one more group XIII atom: preferably, aluminum-containing compounds and one or more indole derivatives. These can form an aluminum coordination organometallic compound with a N-donor indole hub to act as the catalyst activator for the said activity [63,64]. Indole-based organometallic catalysts are quite rare in the literature; however, aromatic indenoindole derivatives, especially 6 and 10-substituted compounds, act like metallocenes rather than N-donor heterocycles by incorporating the π-electron density of the five-membered ring; they are attached directly to the pyrrole ring with half-sandwiched compounds such as zirconium or hafnium [65]. These catalysts can polymerize olefins in the presence of a dehydrogenation catalyst and olefin polymerization catalyst. The mechanism of these catalysts for the formation of polymer is very interesting and provides a deeper insight into the nature of polyolefin formation. The dehydrogenation catalyst enables *in situ* generation of alkenes from oligomers or solvent; furthermore, these alkenes are incorporated into the polyolefins. Hence, these polyolefins have increased long chain branching and lower density without the use of expensive co-monomers [66–68].

The reason for the small number of studies on benzothiazole derivative-based catalysts employed in the olefin polymerization process may be their adverse effects. Fernald et al. [69] claimed a patent which explains the adverse effects of benzothiazole and some other organic compounds. Solid polymer formation in the triethylaluminum-catalyzed conversion of ethylene to liquid α-olefins is reduced by the addition of various organic inhibitors such as 2-mercaptobenzothiazole, phenothiazine, diphenyl amine, quinoline, benzyl disulfide, and thiobenzanilide. The addition of 2-mercaptobenzothiazole inhibits polymer formation without any substantial adverse effect on the efficiency of the process.

Another type of ligand studied for access to active olefin polymerization catalysts derived from benzothiazole is represented by suitable substitution at the 2- position and should have suitable donor atom(s). These ligands offer interesting alternatives to unsubstituted benzothiazole ligand as they can coordinate through the heterocyclic nitrogen atom to stabilize the components of early transition metal complexes. The series of benzothiazole, benzoxazole, and benzimidazole-derived non-metallocene organometallic catalysts **39**–**41** have been employed for olefin polymerization, particularly for ethylene, with greater efficiency and yield when activated with organo-aluminum co-catalysts [50]. Bulkier substitutions at the 2- position of these benzo-fused five-membered heterocycles yield efficient olefin polymerization catalysts when made to react with alkyl or aryl transition metal salts using the appropriate solvent and stoichiometry. Substitutions such as E1, E2, D1, D2, and X are the same as those mentioned for imidazole. The transition metals used were selected from groups III to IX, and alkyl or aryl groups attached to metal ions were methyl, ethyl, benzyl, phenyl, etc. The benzothiazolyl group seems to stabilize the active metal centers to achieve the high productivity, good monomer incorporation, and narrow molecular weight distribution characteristics of a single sited catalyst. This activity mainly depends on the substitutions on the heterocycle, nature of the metal, and aluminum co-catalyst used for the investigation.

There have been relatively few studies on N-donor benzoxazole and benzothiazole-derived ligand systems compared to those on benzimidazole derivatives. A great number of types of benzimidazole-derived ligand systems are in use as olefin oligo/polymerization catalysts. These catalysts may encompass mono, bi, or bis-benzimidazole derivatives for the said activity with different organo-aluminum co-catalysts. Recently, N-donor benzimidazole-derived transition metal catalysts have also been proved to be efficient catalysts for ring-opening polymerization of cyclic olefins such as norbornene as well as for stereospecific polymerization of 1,3-butadiene [70,71]. With similar ligands, chromium halide catalysts are efficient for ethylene oligomerization and polymerization [72,73]. However, their organometallic counterparts have been studied to a lesser extent with the focus more on coordination catalysts. Similar to imidazole derivatives, benzimidazole-derived non-metallocene organometallic catalysts also have two types of coordination modes from either sp^2 or sp^3 hybridized ring nitrogen atoms. If the sp^3 hybridized nitrogen atom is involved in the coordination, than it should be via deprotonation as in case of imidazoles. The olefin polymerization catalysts derived from benzo-fused five-membered heterocycles with two heteroatoms are shown in Fig. 9.

As explained for imidazole-based organometallic catalysts, Gibson et al. extended their work on catalysts with ligands bearing mono and bis-benzimidazole hubs for the conversion of simple olefin monomers into polymers. They reported a different kind of series of alkene-vanadium catalysts for the conversion of olefins to give the desired higher olefins in the presence of another similar catalyst system. The bis-benzimidazole ligands for the preparation of vanadium catalyst series **42**–**44** were prepared by the action of methyliminodiacetic acid on 1,2-diamino benzene at the stoichometric ratio. These catalysts can also include one or more other catalysts for polymerizing α-olefins. Such catalysts are preferably other types of transition metal compounds or catalysts such as transition metal compounds of the type used in conventional Ziegler–Natta catalyst systems or heat-activated supported chromium oxide catalysts of the Phillips type. In order to activate the catalyst systems for olefin polymerization, the co-catalysts may also be used in conjugation with other catalysts to produce only 1-olefins; hence, selected higher olefins like the Schulz-Flory distribution of 1-olefins can be produced. These catalysts further provide a process for the polymerization and co-polymerization of 1-olefins, cycloolefins, or dienes; this involves contacting the monomer under polymerization conditions. Examples of the monomers used for polymerization by **42**–**44** are ethylene, propylene, butane, hexane, styrene, and conjugated or non-conjugated dienes. Suitable monomers for use in making co-polymers using these catalysts are ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, 1-octene, norbornene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, vinyl acetate, vinyl chloride, and styrene.

On the other hand, mono-benzimidazole derivatives not only form stable coordination catalysts with transition metals but can also chelate to alkyl aluminum salts to form stable organo-aluminum catalysts for the ring-opening polymerization of ε-caprolactone [74]. The benzimidazole-based ligand is prepared by the action of 2-(1*H*benzo[*d*]imidazol-2-yl)quinolin-8-amine [75] on 2-hydroxybenzaldehyde in ethanol followed by the addition of acetic acid. The five coordinated mono-alkyl aluminum catalysts **45**–**49** show little activity towards the ring-opening polymerization of ε-caprolactone in the presence of different amounts of benzyl alcohol. These aluminum catalysts may be less active because of their geometry: the square pyramidal geometry around Al is unfavorable for further reaction of Al–Me with alcohol because of the *trans*-position occupied by Al–Me. Another important reason for the lower activity is that the less steric behavior of the ligands favors monomer activation less; the bulky ligand prevents the carbonyl oxygen of caprolactone from coordinating to the Al center, which results in increased electrophilicity at the carbonyl carbon. Hence, a very low activity was observed [76].

3.5. Summary of polymerization results obtained by N-heterocyclic organometallic catalysts of five-membered ring system

It is a challenge to summarize the polymerization results obtained by various research groups by using different complexes, because polymerization behaviors and resulting polymer properties change significantly according to diversified polymerization parameters such as catalyst amount, type and amount of co-catalyst, temperature, pressure, solvent, and co-polymerization. To help the reader to categorize the large array of polymerization catalysts presented in this section, a summary of selected catalysts discussed is given in Table 1. This table should be used as an indicator of activity trends, rather than an absolute measure of catalyst performance, since the activities are subject to polymerization conditions that may not have been optimized. As expected, it is clear that a systematic design of ligand structure considering the steric protection of active sites plays a crucial part in the achievement of highly active catalyst producing high molecular weight polymers.

4. Single-site N-heterocyclic organometallic catalysts containing six-membered ring system

Non-metallocene organometallic catalysts encompassing six-membered heterocyclic ring systems have been used as efficient and interesting catalysts for the past few decades. A large number of six-membered heterocyclic catalysts can be found in the literature; however, the scope of this review was to cover six-membered N-heterocyclic catalysts with one and/or two nitrogen atoms as hetero members. The main example of this class of heterocyclic ligands, around which all heterocyclic catalysts are gyratory, is pyridine; subsequently, a few pyrimidine and triazine derivatives were also focused on. The chemistry behind the selection of six-membered N-heterocyclic ligands as the main backbone for the preparation of catalysts desired for olefin oligo/polymerization is their chelation capacity through heteroatom, which is more basic than that in five-membered ring systems such as pyrrole, imidazole, etc. Numerous studies are going on in this particular field of catalysis across the world, as they are beneficial in the preparation of desired polymeric products useful for mankind.

4.1. Pyridine-based catalysts

Encouraged by the highly active characteristics obtained from complexes ligated by pyridine backbone, these catalysts are now being synthesized in large numbers and indeed showing good to high activities in olefin, especially for ethylene and propylene oligo/polymerization. Pyridine derivatives, especially the substitutions at 2- and/or 2,6-, are extensively used as ligands/ligand precursors for the preparation of catalysts catalyzing

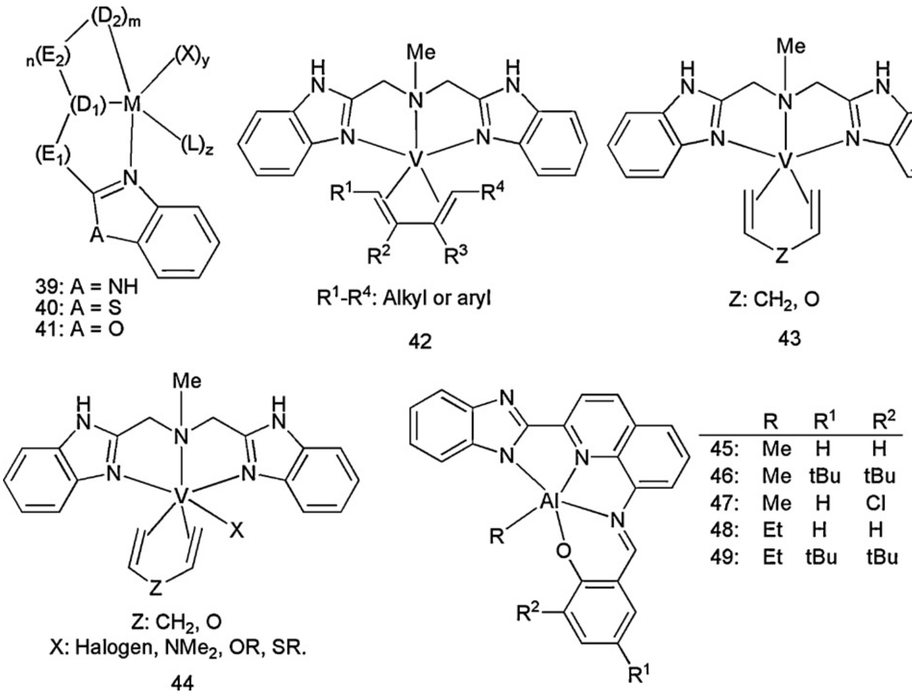


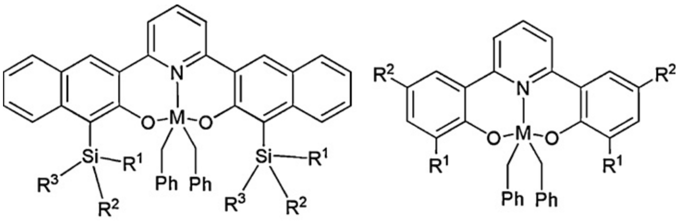
Fig. 9. Olefin polymerization catalysts derived from benzo-fused five-membered heterocycles with two heteroatoms.

olefin oligo/polymerization. Sterically demanding 2-imino and 2,6-bis-imino pyridine ligands impart early transition metals (e.g., zirconium, hafnium, niobium) and late transition metals (e.g., iron, ruthenium, palladium, etc.) with very high catalytic activities for olefin oligo/polymerization; in some cases, the activity is unpredictably higher as in metallocenes. These types of imine ligands have long been reported in the literature; however, their study was restricted only to the preparation and characterization until the 1980s. Stoufer et al. [77] were the first to report the preparation of 2,6-bis-imino hydrazone, which was later developed by many research groups [78–80]. These ligands are readily accessible from the condensation of pyridine-2,6-dicarboxaldehyde or

Table 1
Polymerization results obtained by selected single-site *N*-heterocyclic organometallic catalysts containing five-membered ring system.

M[a]	Complex	Amount (μmol)	MAO (equiv.)	Solvent	*T* (°C)	*P* (atm)	Time (min)	Yield (mg)	R_p[b]	$M_w \times 10^{-4}$	M_w/M_n	Ref.
E	**9**	10.0	1000	Toluene	25	1	30	1.8	0.36	40.5	165.0[c]	[38]
E	**9**	10.0	1000	Toluene	50	1	30	8.2	0.82	69.0	140.0[c]	[38]
E	**9**	10.0	1000	Toluene	25	4	45	10.6	5.65	30.2	110.0[c]	[38]
E	**9**	10.0	1000	Toluene	50	4	22	3.7	4.06	55.6	150.0[c]	[38]
E	**10**	5.0	0[d]	Toluene	25	1	5	733.0	1760.0	6.3	2.1	[41]
E	**10**	0.5	2500	Toluene	25	1	5	1912.0	22944.0	7.1	2.2	[41]
E	**11**	5.0	0[d]	Toluene	25	1	5	874.0	2096.0	9.6	12.2	[41]
E	**11**	5.0	250	Toluene	25	1	5	257.0	616.0	3.6	6.7	[41]
E	**12**	7.6	1000	Toluene	r.t.[e]	1	120	395.0	52.0	n.r.[f]	n.r.	[44]
E	**13**	2.1	1000	Toluene	r.t.	1	120	103.0	49.0	n.r.	n.r.	[44]
E	**14**	3.5	1000	Toluene	r.t.	1	120	22.0	6.40	n.r.	n.r.	[44]
E	**15**	8.7	1000	Toluene	r.t.	1	120	50.0	5.70	n.r.	n.r.	[44]
E	**20**	15.0	400	Toluene	25	1	60	120.0	4.00	n.r.	n.r.	[48]
E	**30a**	50.0	500	Hexane	50	8	60	67.0	0.18	208.8	2.9	[58]
E	**30a**	50.0	500	Toluene	50	6	60	18.0	0.06	n.r.	n.r.	[58]
E	**30a**	50.0	500	Heptane	50	6	60	47.0	0.16	n.r.	n.r.	[58]
E	**30b**	50.0	500	Heptane	50	6	60	15.0	0.05	n.r.	n.r.	[58]
E/H[g]	**30a**	50.0	500	Hexane	60	8	60	86.0	0.22	29.4	1.9	[58]
E	**30d**	50.0	500	Hexane	40	8	60	32.0	0.08	90.5	2.4	[59]
E	**30d**	50.0	500	Hexane	50	12	60	54.0	0.09	366.0	5.4	[59]
MA	**21**	10.0	none	CH_2Cl_2	50	–	240	96.1[h]	–	36.4	3.6	[49]
MA	**22**	10.0	none	CH_2Cl_2	50	–	240	95.0[h]	–	30.1	3.9	[49]
MA	**23**	10.0	none	CH_2Cl_2	50	–	240	99.0[h]	–	13.8	5.5	[49]

[a] Type of monomer: E—ethylene, H—1-hexene, and MA—methyl acrylate.
[b] Rate of polymerization in kg-polymer mol^{-1} h^{-1} atm^{-1}.
[c] High polydispersity induced by multiple active sites.
[d] Co-catalyst: 10 μmol of $B(C_6F_5)$ combined with 0.25 mmol of Al^iBu_3.
[e] Room temperature.
[f] Not reported.
[g] E/H co-polymerization with 3 ml of H.
[h] Conversion (%) of monomer.



	M	R^1	R^1	R^3
50:	Ti	Ph	Ph	Ph
51:	Ti	Me	tBu	tBu
52:	Zr	Ph	Ph	Ph
53:	Zr	Me	tBu	tBu
54:	Hf	Ph	Ph	Ph
55:	Hf	Me	tBu	tBu

	M	R^1	R^2
56:	Ti	CMe_3	CMe_3
57:	Ti	CEt_3	Me
58:	Zr	CMe_3	CMe_3
59:	Zr	CEt_3	Me

Fig. 10. Group IV mononuclear organometallic catalysts derived from a pyridine core with O_2N donor set.

2,6-diacetylpyridine with two equivalents of the corresponding aniline in an alcohol followed by the addition of an acid such as acetic or formic acid. In a similar manner, 2-imino pyridine ligands can be prepared by using pyridine-2-carboxaldehyde or 2-acetyl pyridine instead of 2,6-di substituted derivatives. Recently, a few *N*-aryl fused cyclic-aryl derivatives of 2,6-bis-imino pyridines have also been reported for the preparation of transition metal complexes [81,82]. Conversely, 2- or 2,6-bis imino pyridines formed by the condensation reaction of 2,6-diamino pyridine with one or two equivalents of aldehyde/ketones have also been reported in the literature; however, their study did not involve the oligo/polymerization of olefins [83]. Not only imine pyridine derivatives but also amides, amines, etc. are active catalysts for olefin oligo/polymerization with defined substitutions. The reactivity of 2,6-bis and 2- substituted pyridines with transition metals to form stable olefin polymerization catalysts are discussed in detail with respect to each metal from groups IV to X in the following paragraphs.

Recently, many studies have reported on the innovation of efficient group IV organometallic catalysts for the title activity. 2,6-Bis-naphthoxy substituted pyridine derivatives were efficient for the preparation of stable group IV discrete mononuclear organometallic catalysts **50**–**55** with an O_2N donor set, as shown in Fig. 10. The activity was better due to the presence of a triphenyl/tert-butyldimethyl silane substitution adjacent to the donor group (-OH) present in the naphthyl substitution [84]. These organo-silyl substitutions were better hindering groups around the metal ion and proved to produce significant yields of oligomers of the desired composition. On the other hand, these ligands provide two different coordination modes to give rise to two stable stereoisomers in neutral compounds. Coordination catalysts of the same ligands were good for oligo/polymerization of propylene; however, their dibenzyl counterparts were inadequate when $[Ph_3C][B(C_6F_5)_4]$ was used as the activator. In the series of catalysts **50**–**55**, only zirconium precursor **53** was active when activated with MAO (1000 equiv vs. Zr). However, the activity of the **53**/MAO system (320-490 $kg.mol^{-1}.h^{-1}$) was at least one order of magnitude inferior to that of related systems based on pyridine-bis(phenoxy) zirconium dibenzyl complexes **56**–**59** [85,86]. These zirconium and titanium catalysts **56**–**59** supported by novel tridentate, bis(phenolate)pyridine donor ligands were prepared [87] and investigated for applications in propylene polymerization. Both titanium and zirconium complexes were active for the polymerization of propylene upon activation with MAO. The activities observed for the zirconium catalysts **58** and **59** were excellent at more than 10^6 g polypropylene/(mol Zr h). The excess of MAO affects the polymerization activity and level of β-H elimination and chain transfer events. However, titanium systems **56** and **57** are about 10^3 less active but generate polymers of higher molecular weight [85].

Mixed substitutions (with respect to the above paragraph) at the 2- and 6- positions of pyridine means that naphthyl and phenoxo substitutions at the 2- and 6- positions also yield effective titanium(IV) benzyl catalysts for the polymerization of ethylene, as reported recently [88]. Titanium catalysts **60**–**64** (Fig. 11) and the hafnium catalyst **65** show excellent ethylene polymerization activity due to substituents that are seemingly remote from the active site upon the olefin polymerization characteristic. These catalysts are subjected to ethylene polymerization at 100 °C; the titanium catalysts have good to excellent activities for such a high polymerization temperature. Linear polyethylenes displaying high M_w values are produced at this higher temperature; however, the associated molecular weight distributions (6.7 for **62** and 2.9 for **63**) are not indicative of active site uniformity [89]. Ethylene or propylene co-polymerization tests have also been studied for catalysts **60**, **61**, **62**, and **64**. Significantly lower activities and M_w values were observed for **60** and **61** (i.e., $M_w/M_n = 5.3$ and 5.8, respectively), while there is evidence of multimodality for **62** and **65**. These results also signify that for the [O, N and C] system, incorporation of a bulky σ-aryl substituent in the immediate vicinity of the metal core can lower catalytic efficiency rather than sustain the polymerization reaction. Recently, a dimethyl hafnium(IV) complex was conveniently prepared and examined for the propylene polymerization. The catalyst has a direct Hf-C linkage from a carbon atom present at the naphthyl substitution at the 2- position of the pyridine ring. The pyridylamido Hf complex **66** with a C_1 symmetric chiral structure is effective for isospecific propylene polymerization [90,91]. Kress et al. reported [92] the preparation of a series of zirconium-benzyl complexes for a tridentate C_2-symmetric dialkoxo ligand [93]. These catalysts were efficient and illustrated diastereo-selectivity in olefin single-insertion reactions. These active catalysts can be prepared by the action of tetrabenzyl zirconium on tridentate, a C_2-symmetric, stereochemically rigid dialkoxo 2,6-bis[(1*S*,2*S*,5*R*)-(−)-menthoxo]pyridyl ligand. Notably, zwitterionic and cationic benzyl complexes (**67**–**69**) insert one molecule of α-olefins into their zirconium–carbon bond, leading to spectroscopically distinguishable diastereoisomeric complexes. Aromatic free alkyl complexes **67**–**69** may lead to higher insertion stereoselectivities and actual polymerization activity.

Bidentate pyridine ligands with donor groups at the 2- position can also form stable and efficient group IV organometallic catalysts for olefin oligo/polymerization. The representative catalysts structures are shown in Fig. 12. In such cases, the metal-to-ligand (except auxiliary ligands) ratio is usually 1:2 or 1:3 depending on the nature of the minor ligand(s) attached to the metal. Recently, Pellecchia et al. reported [94–96] a series of amidomethyl pyridine derivatives for the preparation of zirconium catalysts. Among many, the dibenzyl catalyst **70** showed good activity towards ethylene polymerization. The addition of the dibenzyl catalyst preactivated with $[Ph_3C][B(C_6F_5)_4]$ in a toluene solution containing triisobutylaluminum as a scavenger and saturated with the monomer. GPC analysis of the formed polymers disclosed a monomodal, although a still broad molecular weight distribution was observed. The series of tri-benzyl attached zirconium catalysts **71**–**73** were reported as active catalysts for the co-polymerization of ethylene [97]. Higher activities can be achieved for the co-polymerization of ethylene with 1-hexene using these catalysts. The activity is strongly dependent on the size of the aryl substituent at the 2- and 6- positions of the pyridine ring. The highest activity was observed for **71**, whereas the more and less bulky substituents **72** or **73**, respectively, result in greatly reduced activities. The related hafnium complexes **74**–**76** encompassing similar ligand systems with a variety of co-catalysts were also employed in the co-polymerization of ethylene with

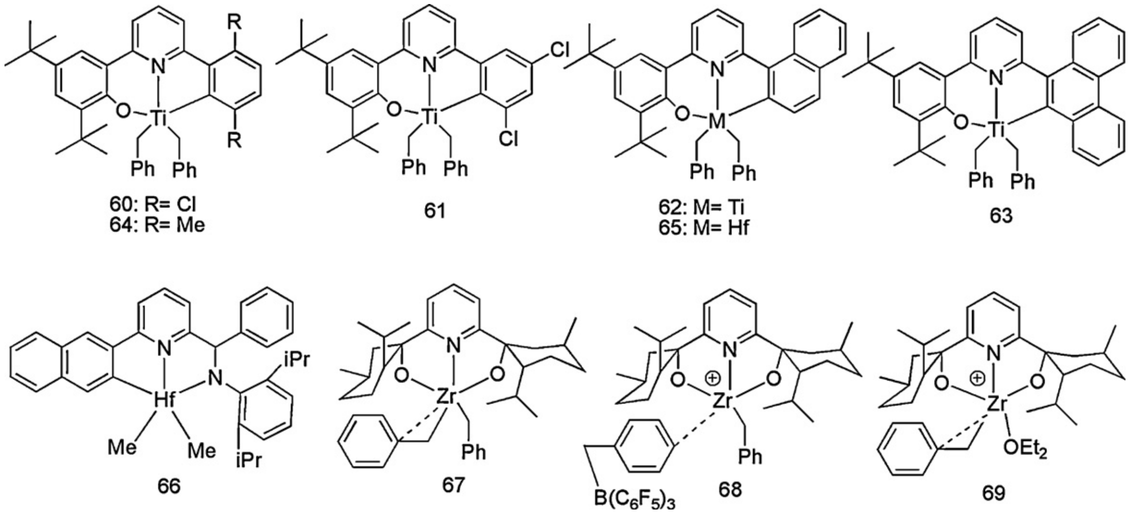


Fig. 11. 2,6-Disubstituted non-metallocene group IV organometallic catalysts derived from pyridine.

styrene and 1-octene [96,97]. A similar kind of activity was also recorded for group IV tri-benzyl catalysts with other heterocyclic cores such as tetrahydro furan [96,97].

Mono-imine derivatives of 2,6-diacetyl pyridine formed stable organometallic catalysts suitable for ethylene polymerization. Sommazzi et al. claimed many such related breakthroughs in their patent [98]. This group demonstrated the preparation of said ligand systems by reacting 2,6-diacetyl pyridine with different substituted anilines at a 1:1 ratio to get mono-imine derivatives of the pyridine ligands with a free acetyl group at the 6- position; this in turn reacts with suitable organometallic precursors to form the respective catalysts. The possible coordination sites are NNO from the imine, pyridyl, and acetyl groups. The metals are selected from groups III–XII, and the organic part attached to the metal ion could be linear, cyclic, or branched alkyl groups with 1–20 carbon atoms. These catalysts are employed not only for ethylene polymerization but also for the co-polymerization of α-olefins.

Neutral and cationic di and mono isobutyl substituted zirconium **77** and **78** and hafnium **79** and **80** catalysts were prepared from a 2-trisubstituted pyridine derivative and well-organized initiators for the polymerization of 1-hexene [99,100]. These alkyl complexes are stable towards β-hydride elimination even below 10 °C and active initiators for the living polymerization of 1-hexene. The cationic zirconium diamido [101–104] donor systems investigated for β-hydride elimination may be slow in part due to steric reasons.

Both mono and bi-substituted derivatives of pyridine react vigorously with group V metals to form the desired olefin polymerization catalysts (Fig. 13). Homogeneous systems based on group V metals have come under much less study than group IV congeners with pyridine-based ligands specifically. The initial approach to the design of catalytic precursors involving vanadium, niobium, and tantalum was to exploit the uses of these catalyst systems for the title activity. The synthesis of new efficient group V catalysts, specifically, vanadium complex catalysts, for controlled olefin polymerization has thus been one of the most attractive targets for recent studies. There have been many reports, especially on vanadium(III), vanadium(IV), and vanadium(IV) complexes, for the polymerization of olefins with/without an anionic ancillary donor ligand. Interestingly, a 2,6-bis(imino) pyridine derivative ligand directly involved in the reactivity of the metal center became a key to understanding the high activity of the catalytic system derived from vanadium [105]. The ligand system was isolated as a bis-imine compound upon reaction with 2,6-biacetyl pyridine on 2,6-diisopropyl aniline at a 1:2 molar ratio [106]. Dimethyl vanadium(I) catalysts **81** and **82** were isolated (in crystalline form) from the tridentate ligand as an active species; they were stabilized by tetramethylenediamine (TMEDA). Novel catalysts act as potent ethylene polymerization precatalysts, and polymers produced by the complex activated with PMAO showed a bimodal character in the GPC. Alkylation of the pyridine ring transforms the initial coordination complex into a covalent transition metal amide; the process is accompanied by a decrease in the coordination number of the vanadium center. Steric hindrance is probably responsible for the very poor co-monomer incorporation observed with this system. Further attacks on the ligand, which reduces the metal towards an inactive vanadium(I) square pyramidal species [107], is very fast with MeLi and may also occur at a smaller extent with a methyl aluminum co-catalyst. Despite the involvement of the ligand part in the reactivity of the metal center; it is strongly bound to the metal with no evidence that it could be abstracted by the Al co-catalyst. According to the authors [108], this is the unique ability of this ligand to stabilize vanadium alkyls and is probably responsible for the high activity observed in this system. Similarly, the same vanadium catalysts bridged by dinitrogen (end-to-end

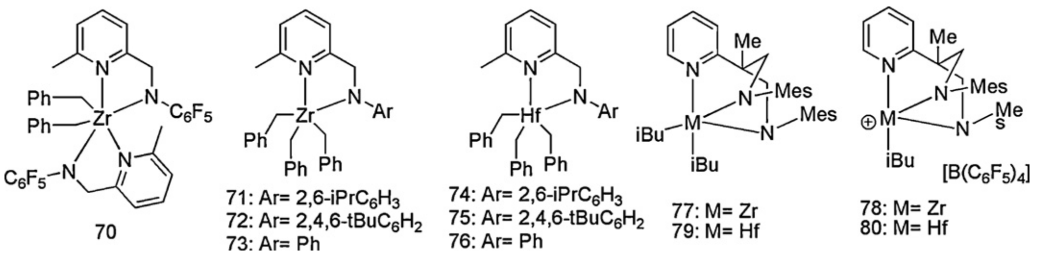


Fig. 12. Group IV non-metallocene organometallic catalysts derived from pyridine ligands with donor groups at the 2- position.

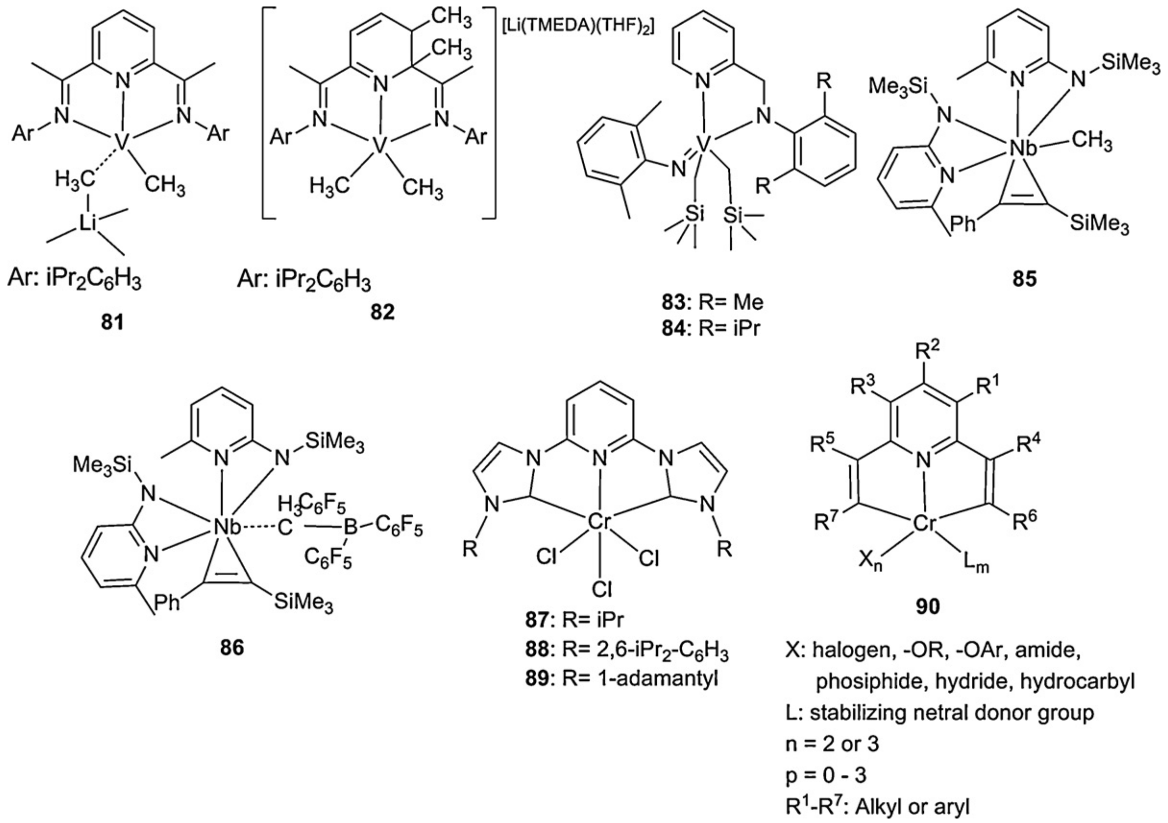


Fig. 13. Non-metallocene organometallic group V and VI catalysts with pyridine scaffold.

mode) were efficient catalysts for ethylene polymerization [109]. Many of the alkyl vanadium catalysts with different oxidation states are available in the literature; they use 2- substituted pyridine as a chelating core with higher activity towards olefin polymerization [110–114]. Di(trimethylsilylmethyl) vanadium(V) complexes have been prepared by the action of $LiCH_2SiMe_3$ on the dichloro counterpart of vanadium(V) complexes, and their structures have been established by X-ray crystallography [115]. Chloro counterparts of these catalysts were effective catalyst precursors for ethylene polymerization in the presence of aluminum co-catalysts, and catalytic activities were up to 6000 kg PE/mol V h in the presence of Et_2AlCl. However, the di(trimethylsilylmethyl) vanadium(V) complexes **83** and **84** were effective for ring-opening metathesis polymerization (ROMP) of norbornene in benzene at 80 °C in the presence of PMe_3. This is the beauty of organometallic catalysts that cannot be found in simple coordination catalysts. However, the polymer yields are low, and the hurdle is the reaction condition, i.e., the reaction does not proceed in the absence of PMe_3. ROMP does not occur in the absence of PMe_3 under the same conditions [116–119], suggesting that an additional coordination of PMe_3 may be required to induce α-hydrogen elimination. Another interesting fact about these catalysts is that the presence of a pyridine moiety in the chelate ligand system in **83** and **84** clearly cannot initiate α-hydrogen elimination; thus, the octahedral geometry formed by coordination of an additional donor ligand may be required to induce α-hydrogen elimination at the elevated temperature.

Until now, niobium compounds in general have been very rarely applied for the polymerization of olefins despite their moderate cost, limited toxicity, and large availability of stable oxidation states, which make them versatile precursors [15]. Textured non-metallocene organometallic niobium catalysts are even more rarely found in the literature for the title activity. Significant improvements in norbornene ROMP have recently been achieved by many researchers; meanwhile, for ethylene polymerization, the optimization process of niobium-based catalytic systems still needs improvement. 6-Methyl-2-trimethylsilylaminopyridine ligand acts as a bidentate monobasic chelate towards niobium(V) salt and forms an active niobium catalyst **85** for ethylene polymerization. Furthermore, an addition compound is obtained by the reaction of **85** on $B(C_6F_5)_3$ to yield aminopyridinato zwitterionic compound **86**. This may be due to the extremely interesting applications of the latter compounds in olefin polymerization or in selective couplings of α-olefins for organic synthesis [15,120,121]. Apart from these, trichlorotantalum(V) and trichloroniobium(V) catalysts with mono and bi-substituted pyridine ligands also have well-organized systems for ethylene polymerization in combination with aluminum co-catalysts and show very high activity among their analogues [122–125].

Designing efficient organometallic group VI metal catalysts—especially the search for chromium-based non-metallocene polymerization catalysts for olefin coordination polymerization and new catalysts for the production of linear α-olefins from ethylene—has attracted considerable attention in the last few years. Heterogeneous polymerization catalysts based on Cr are well established in the form of the Phillips and union carbide systems (Cr/SiO_2); much interest in Cr-based polymerization catalysts with the pyridine ring should arise from these technologies. Besides polymerization, chromium-based catalysts capable of selective trimerization and tetramerization of ethylene to 1-hexene or 1-octene have revolutionized olefin oligomerization [126], as these products have enormous potential for applications in the manufacture of desired polymers. However, few articles are available on the topic of depicting the formation of non-metallocene organometallic catalysts with a pyridine hub. Among these papers, most are in the form of patents in the literature.

Gibson et al. [127] described a new class of exceptionally active Cr(III) organometallic catalysts for the production of α-olefins based on tridentate pincer ligands containing heterocyclic carbene donors; these encompass pyridine-2,6-bis(3-imidazoline) substitutions. While the rapid development of catalysts based on heterocyclic carbene ligands (also called bis-carbene derivatives [128]) has been ongoing for over a decade, these results represent the first time that this ligand class has been employed to produce highly active catalysts for olefin oligo/polymerization reactions. These results extend the usefulness of these flexible ligand systems, and their potential to act as subsidiary ligands for early transition metal olefin polymerization, especially with chromium, seems promising. Cr(III) catalysts **87**–**89** of these ligands in combination with MAO give exceptionally active catalysts for ethylene oligomerization. Complexes **87** and **88** give rise in each case to a Schulz-Flory distribution of α-olefins and are well characterized. Gabbaï et al. [129] investigated the preparation process and mode of action in ethylene polymerization of a pentaflorobenzyl-substituted chromium catalyst with unsubstituted pyridine as a minor ligand. The catalyst is thermally stable and shows higher polymerization activity as a single-component ethylene polymerization catalyst than previously reported neutral chromium complexes [130]. However, the methyl counterparts of the same ligand without thee pyridine ligand end up in the formation of low molecular weight oligomers obtained from ethylene [131,132]. This implies the significance of both the presence of the ligand ring and the bulkier aromatic benzyl substitution to the chromium center.

The interest in non-metallocene polymerization catalysts has led to increased activity in the synthesis of well-defined chromium-based paramagnetic organometallic complexes and resulted in a number of patents. The remarkable pace of research is exemplified by Alfred *et al.*, who in their European patent [133] discussed numerous chromium-based non-metallocene organometallic catalysts for the polymerization of α-olefins. Numerous pyridine 2,6-bisimine ligands with various substitutions at 3-, 4-, 5-, and/or on amines were prepared, and suitable ligand precursors were found for the preparation of alkyl chromium catalysts to in turn enable the polymerization of α-olefins. The general structure of the alkyl/aryl chromium(II or III) catalysts **90** illustrates the formation of a series of five or six coordinated catalysts with the tridentate bis-imine ligand system. These pyridine bis-imine based ligand systems have been employed for the preparation of polymerization catalysts over the past several years; they appear to be part of an increased interest in the synthesis and reactivity of well-defined paramagnetic organometallic complexes of first-row transition metals, especially with chromium. These organo-chromium catalysts in combination with organo-aluminum activators can polymerize α-olefins over a temperature range from −50 to 300 °C. This type of process has been applied to the manufacture of homo or co-polymers of ethylene comprising at least 90 mol% of units derived from ethylene. Among the disclosed, methyl chromium(II or III) catalysts bearing tetrahydro furan as auxiliary ligand were effective catalysts for the polymerization of α-olefins in the temperature range 30–115 °C. Similar efforts have been reported by Luis et al. for which they claimed a European patent [134]. These researchers reported a convenient method for the preparation of chromium(III) alkyl and aryl catalysts suitable for the (co)polymerization of α-olefins in combination with aluminum-based co-catalyst systems as activators. The molecular weight of the polyethylene obtained by these chromium(III) catalysts varies between 1000 to more than 100,000, depending on the architecture of the catalysts used.

Bidentate pyridine ligands with sulfur or phosphoros substitutions (Fig. 14) are noted for the preparation of stable olefin polymerization catalysts. A different class of 6-phenylpyridines with alky/aryl substituted phosphenes at the 2- position have been studied and used as ligands for the preparation of alkyl/aryl chromium catalysts meant for olefin oligomerization. This series of ligands are of great interest due to their ligand architectures and efficiency for the oligomerization of olefins, especially ethylene.

A series of alkyl/aryl chromium catalysts with ligand systems **91**–**93** were patented by Ackerman et al. [135]. They claimed a method of producing oligomers of olefins comprised of reacting olefins with a catalyst under oligomerization conditions. The catalysts were prepared by reacting a chromium precursor with pyridyl ether (**91**), pyridyl thioether (**92**), and pyridyl phosphino (**93**) ligands. The metal precursor used in the method of the present invention can be selected from the group consisting of $(THF)_3CrMeCl_2$, $(THF)_3CrCl_3$, $(Mes)_3Cr(THF)$, $[\{TFA\}_2Cr(OEt_2)]_2$, $(THF)_3CrPh_3$, and $(THF)_3Cr(\eta^2\text{-}2,2'\text{-Biphenyl})Br$. The resulting pyridylphosphino compounds **94**–**96** can be used to trimerize or tetramerize ethylene to 1-hexene, 1-octene, or mixtures of the two. At the same time, they also claimed another patent [136] on active chromium catalysts for the same oligomerization of olefins by replacing the phosphorus with oxygen or sulfur **97**–**100** to produce numerous pyridine ether and thioether catalysts. The above-mentioned alkyl/aryl chromium salts are reacted with **97**–**100** to obtain the desired alkyl/aryl chromium catalysts. Chromium pyridyl ether and thioether catalysts are effectively used as an oligomerization catalyst for ethylene like phosphene catalysts. Like phosphene-based pyridyl systems, ether and thioether catalysts are also involved in the tri and tetramerization of ethylene into 1-hexene and 1-octene. The dimerization of α-olefins, especially ethylene, into 1-butene has been found for some tungsten-based organometallic N-donor homogeneous catalysts [137]; however, there is nothing in the literature on pyridine-based N-donor non-metallocene organometallic catalysts based on molybdenum or tungsten for the title activity.

Efforts to develop alternatives to group IV metallocene single-site olefin polymerization catalysts have resulted in major breakthroughs with group VII metals as well. To expand the understanding of the unique behavior of mono and bi-substituted pyridine derivatives as important ligand systems, many research groups have investigated the behavior of manganese derivatives. Given the high activity of vanadium and iron derivatives, an alkyl/aryl Mn(II) diiminopyridinate complex can also be expected to be another potent catalyst series. On the other hand, divalent manganese alkyl complexes are stable species, and a substantial number of homoleptic derivatives have been reported in the literature [138]. Furthermore, the activity is expected because the coordination geometry of manganese is identical to that of iron and cobalt "supercatalysts" (explained in the forthcoming section) with the same distorted square pyramidal arrangement and coordination geometry defined by two alkyl/aryl groups and three nitrogen donor atoms of the tridentate 2,6-disubstituted pyridine-based ligand.

Gambarotta et al. [139] reported the synthesis of mono- and zero-valent manganese alkyl complexes containing the diiminato pyridine ligand and demonstrated that alkyl substitution stabilizes the compound at the expense of catalytic performance. The reaction of $MnCl_2(THF)_2$ with tridentate pyridine ligand in toluene is a straightforward complexation reaction that produces a five-coordinate dichloro Mn complex with NNN donor sites (**101**) (Fig. 15). However, **101** does not exhibit ethylene polymerization activity upon activation with methylalumoxane (Mn:Al 1:1000) or other co-catalysts under standard reaction conditions. This inactivity is due to the high-spin d^5 electronic configuration (μ_{eff} 5.74 BM) of manganese, which is obviously responsible for the lack of activity by either preventing alkylation of the manganese center by Al or, more likely, causing instability of the Mn-alkyl function. Thus, **101** is treated separately with 2 and 4 equivalents of MeLi to produce the mono (**102**) and zero valent Mn-derivatives, respectively,

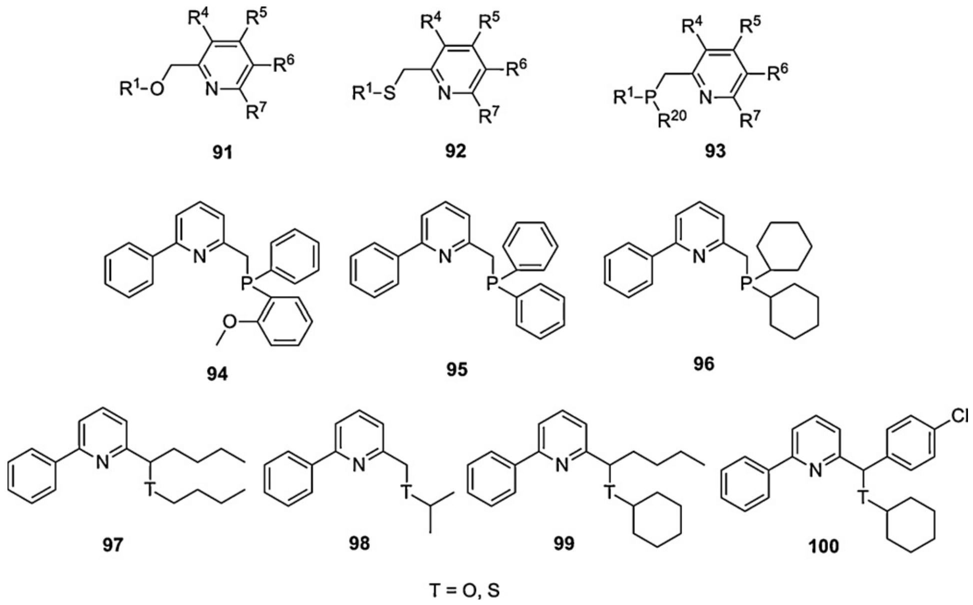


Fig. 14. Bidentate pyridine ligands with ether, sulfur or phosphorus(III) substitutions.

with distorted square planar geometry. Furthermore, **102** can be converted into the trimethylsilylmethyl Mn-derivative **103** by the appropriate methods. This reduction of the metal center is not particularly surprising given that Mn(II) complexes are used as radical initiators for radical polymerization processes [140]. Furthermore, Gambarotta et al. investigated the activity of chromium and manganese(I) derivatives with a binuclear core that do not show any prominent ethylene polymerization activity combination with a variety of co-catalyst; they finally concluded that the easy reduction of the metal center is responsible for the lack of activity [141]. Apart from the above, few alkyl/aryl Mn(II) derivatives with similar ligands of **101** were olefin polymerization and oligomerization agents with activities similar to chromium catalysts.

Many mono/bi-substituted pyridine ligand systems spectacularly enhance the reactivity of electron-rich group VIII metals, especially iron, towards Ziegler-Natta olefin polymerization, which has attracted considerable attention. The very high activity of these catalysts poses some fascinating questions about which particular ligand-to-iron bonding features may be responsible for the tremendous activity of these catalyst systems. On the other hand, the polymers produced by these catalysts encompass a high degree of polymerization and variable polydispersities. Among group VIII metals, iron is the most studied metal with pyridine ligands having alkyl and/or aryl bonding. Numerous routes have been introduced for the preparation of alkyl/aryl/trimethylsilylmethyl iron catalysts employed in olefin polymerization (Schemes 1 and 2). In addition, for bis(imino)pyridine iron-catalyzed reactions for ethylene polymerization, the chelate redox activity presents an additional challenge for determining the oxidation state of iron and understanding fundamental transformations relevant to chain initiation, growth, and termination. Very recently, Chirik et al. [142] reported the synthesis and electronic structure of cationic, neutral, and anionic bis(imino)pyridine iron-alkyl complexes **104**–**110** and evaluated the redox activity of iron in ethylene polymer-

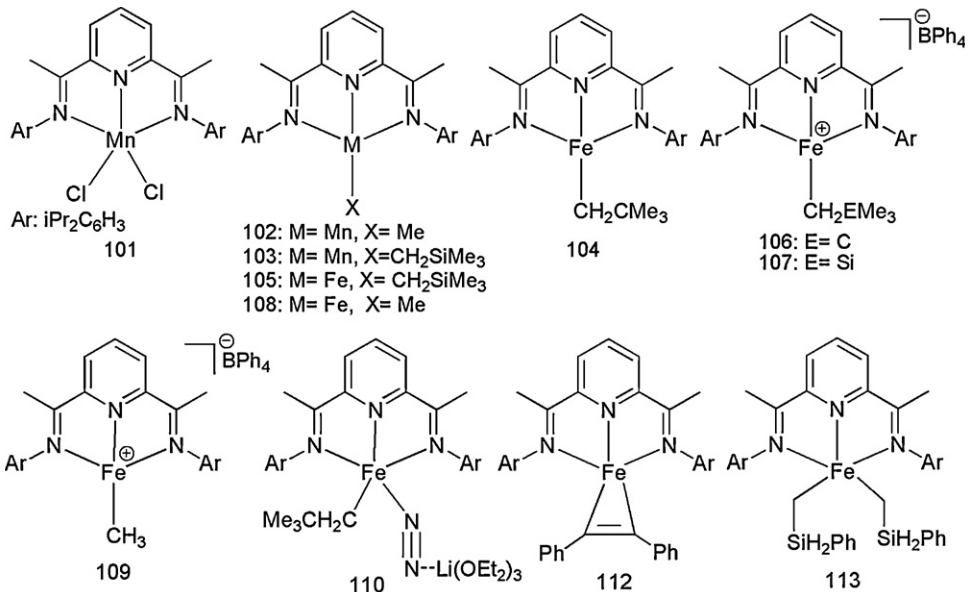
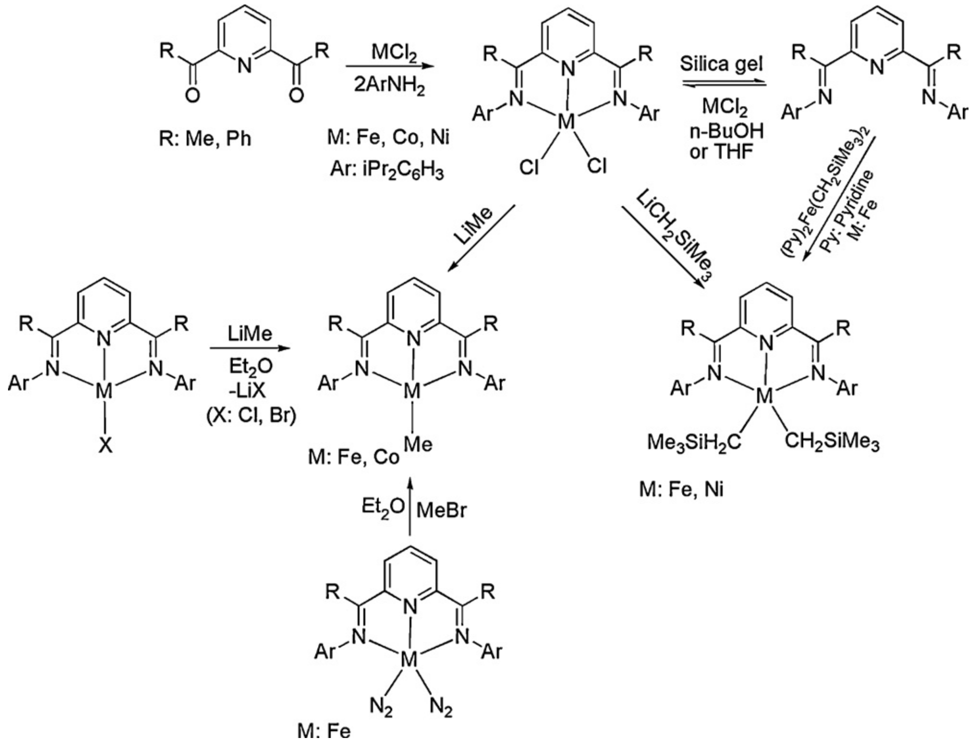


Fig. 15. Non-metallocene organometallic manganese and iron catalysts derived from pyridine backbone.



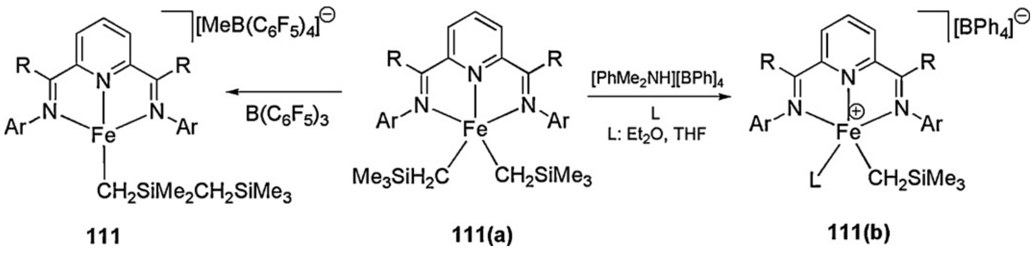
Scheme 1. Preparation of late first row transition metal non-metallocene organometallic catalysts.

ization [143]. The data established high-spin ferrous compounds ($S_{Fe} = 2$) with neutral redox-innocent bis(imino)pyridine chelates. Upon exposure to ethylene, all three types of iron compounds **104**–**110** serve as single-component polymerization catalysts and yield linear polyethylene terminated by olefin end groups arising from β-hydrogen elimination. Furthermore, for **104** and **105**, the neutral and monoanionic forms of the bis(imino)pyridine are a sufficiently weak field that high-spin ferrous compounds result; in contrast, for **106**, **107**, and **109**, the field strength increases sufficiently that a low spin d^6 compound results. The same group has also reported on a new alkyl iron catalyst bearing the tridentate pyridine ligand system as in case of **104**–**110** [142]. The alkyl iron cationic catalyst **111** is prepared by the action of silyl salt on dichloro iron(II) catalyst. Interestingly, **111** catalyzed the ethylene polymerization reaction without the use of any aluminum-based co-catalysts; this may be predicted because of the bulkiness of the alkylsilyl component directly attached to the iron center.

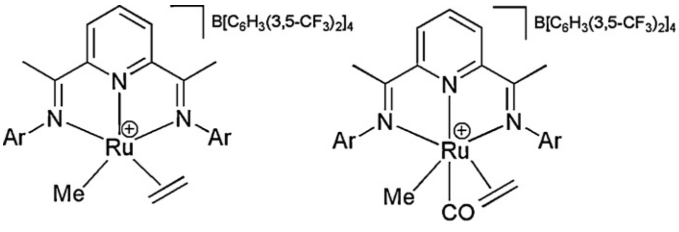
Cationic bis(imino)pyridine Fe(II) complexes of types **104**–**110** (Fig. 15) were made [144,145], but then the synthetic attempts are presented as unsuccessful, and yet, those species are used for polymerization in combination with aluminum co-catalysts like MAO or $AlMe_3/B(C_6F_5)_3$. In the latter case, polyethylenes with narrower polydispersities were obtained, partly due to the absence of chain transfer to aluminum. They were also tested for the copolymerization of ethylene with polar monomers, and although high activity was observed in the presence of methyl methacrylate, no co-polymer was obtained. The dinitrogen iron complexes serve as polymerization and effective precatalysts for hydrosilylation of olefins and alkynes. The putative catalytic intermediates **112** and **113** were active species for the said conversions and were later structurally characterized.

According to research by Gibson et al. and Brookhart et al., alkyl/aryl/alkylsilyl iron catalysts bearing tridentate bis(imino)pyridine support usually show very high catalytic activity for the formation of linear polyethylenes and are responsible for obtaining high-mass polymerization and oligomerization of ethylene depending on the bulkiness of the arylimino groups present on either side of the pyridine hub at the 2- and 6- positions. Besides the alkyl/aryl/alkylsilyl derivatives of the iron catalysts, iron(II) dihalide catalysts modified with 2,6-bis(imino)pyridyl ligands [146–148] act as active catalysts for the polymerization and oligomerization of ethylene on activation by MAO. This has been one of the major breakthroughs in olefin polymerization catalysis over the last few years.

Although non-metallocene organometallic ruthenium complexes active for olefin polymerization, in particular ethylene polymerization, are rare, few research groups have explored the utility of other group VIII metals; ruthenium is the main focus of



Scheme 2. Preparation of cationic iron catalysts with pyridine scaffold.



114
Ar: 2,6-$Me_2C_6H_3$

115
Ar: 2,6-$Me_2C_6H_3$

Fig. 16. Ruthenium catalysts involved in ethylene polymerization.

studies. Brookhart et al. [149] reported the synthesis and isolation of stable cationic ruthenium methyl ethylene complex **114** and the corresponding carbon monoxide adduct **115**, as shown in Fig. 16. However, these complexes fail to serve as effective initiators for the polymerization of ethylene and α-olefins and co-polymerization of olefins and carbon monoxide. Furthermore, the meridional geometry of these ligands necessarily differentiates the remaining binding sites around the metal center to create distinct axial (*cis* to pyridine) and equatorial (*trans* to pyridine) positions, a feature that is lacking in group X metals with similar ligand systems. Hence, the same analogous inactivity of **114** and **115** towards ethylene polymerization is predicted.

Enormous progress in catalysis using molecular group IX non-metallocene organometallic complexes bearing mono or bi-substituted pyridine ligands during the last decade has enabled control of the stereochemistry of poly-α-olefins and the molecular weights of polyethylenes. Fig. 17 explains the structure of group IX non-metallocene organometallic complexes involved in olefin polymerization. These can serve as precursors for single-component olefin polymerization catalysts and also provide insight into the nature of the propagating species. The main focus of this research is to obtain a high activity for producing very high molecular weight polyethylene, living polymerization to control molecular weights, and high or controllable incorporation of co-monomers in the co-polymerization and formation of polyethylene with regulated branching. Among group IX metals, cobalt(II) pyridine catalysts have come under intense focus as they can reach the desired goals of this particular research. Some methyl or allyl rhodium catalysts with bis(imino)pyridine ligand system also exhibits the said activity.

Almost all 2,6-bis(imino)pyridyl Co(II) complexes are green crystalline solids with μ_{eff} at room temperature of 4.6–4.8 BM, which is consistent with the values expected for high-spin Co(II) five-coordinate complexes bearing square-pyramidal geometry as they have all possible nitrogen donor groups in the plan. However, there have been no reports that these are so important to favor spin pairing and give a doublet ground state ($S = 1/2$). Usually, mono or di alkyl/aryl cobalt(II) bis(imino)pyridine catalysts are prepared by the treatment of their respective dihalo cobalt(II) species with LiMe; however, few cases report adverse results in the reduction to produce alkylated cobalt(I) species (**116**) [150–152] similar to iron compounds. Catalyst **116** produces low-activity ethylene polymerization upon activation with Li[B$(C_6F_5)_4$] [150]. A very interesting and different coordination mode is displayed by the ligand **117**, in which coordination is found from the methoxy oxygen and imine nitrogen present outside the coordination sphere in both dichloro and monomethyl cobalt catalysts **118** and **119**. Furthermore, the isomeric mixtures **119** and **120** react at a 1:1 ratio in the presence of excess B$(C_6F_5)_3$ to generate a stable cationic cobalt catalyst. However, the product was not the one expected; it was instead a η^6-arene cobalt cation **121**. This unexpected compound is formed due to the presence of excess B$(C_6F_5)_3$, which leads to cleavage of a Co-N bond and favors arene linkage (Scheme 3). Similarly, the catalytic performances of these catalysts towards ethylene polymerization are even more interesting. Activation of the isomeric mixture **119/120** with Li[B$(C_6F_5)_4$] results in polyethylene formation with an average activity of 36 g mmol(**119/120**)$^{-1}$ h^{-1} bar^{-1}, which is threefold more than the activity executed by **118** when activated with MAO/BF_3. The produced polyethylene has a higher molecular weight (>2000), which is mostly bimodal with broader molecular weight distributions ($M_w/M_n = 1.5$ to 7.6). However, the olefin polymerization pathways of catalyst systems indicate the occurrence of a different activation mode. Furthermore, the lithium cation may interact with one "arm" of the chelate pyridine donor ligand, which would create an open coordination site at a reactive overall cationic reactive intermediate **122**.

Like alkyl/aryl iron(I) bis(imino)pyridine derivatives, cobalt(I) compounds also shows good to moderate activity towards ethylene polymerization. Cobalt(I) catalysts of the general formula **123** were prepared by the dihalo counterparts **124**. Active alkyl catalysts **123** can be produced by action of alkyllithium or alkyl magnetism halide on **124**. Complexes of type **123** do not polymerize ethylene by themselves, but after the addition of excess aluminum co-catalysts like MAO, polyethylene is produced with properties identical to and with activity similar to those of MAO-activated **124**, which implies the presence of the same active species (except **119** and **120** type) [153–155].

The involvement of other group IX metals in assisting olefin polymerization was relatively low. This may be because of the lesser activity towards polymerization and expensive metal salts when compared to cobalt catalysts. Even with the said entities, few rhodium-based catalysts have been employed for olefin polymerization. A series of methyl rhodium(III) bis(imino) pyridine catalysts **126**–**128** were studied by Brookhart et al. [149] for ethylene polymerization. Monochloro rhodium catalyst **125** is reacted with methyliodide and AgOTf to obtain **126**, C_2H_4, NaB$(C_6F_5)_4$, and methyl iodide to obtain **127**; finally, **127** is treated with C_2H_4 and $AgBF_4$ to obtain **128**. Among this series, rhodium complexes **126** and **128** provided even more of a surprise in their structural elucidation. All catalysts were studied for ethylene polymerization; however, these systems once again did not exhibit any activity for polymerization. The main reason for their inactivity is similar to the explanation provided for ruthenium catalysts with the same ligand territories.

Homogeneous systems based on Group X metals have been widely studied more than the other metals in the periodic table. Pertinent catalysts are shown in Fig. 18. The initial approach to the design of the catalytic precursors began almost exclusively from this group of metals. In view of the generally observed increase in the M–L bond energy as one goes down a group of transition metals, platinum catalysts are generally less reactive than nickel and palladium ones. Group X olefin polymerization catalysts can be categorized into two main types on the basis of the donor atom: diimine ligands with N, N donor groups (Brookhart type) and anionic phenoxo ligands with N, O donor groups (Grubbs type). Generally, diimine Ni(II) complexes show higher catalytic activity than the corresponding palladium complexes. The palladium catalysts produce polyethylene with a highly branched structure and the degree of branching can be varied depending on the monomer pressure. The area of ethylene polymerization with late metal catalysts was revitalized when Brookhart et al. [156,106,157,158] invented a family of new cationic Ni(II) and Pd(II) α-diimine catalysts for the polymerization of ethylene, α-olefins, and cyclic olefins like norbornene and the co-polymerization of nonpolar olefins with a variety of functionalized olefins. Since then, a huge number of studies have reported on halo and/or alkyl/aryl/alkylsilyl nickel(II)/palladium(II) catalysts with fascinating activities towards olefin oligo/polymerization. Among the first two group X met-

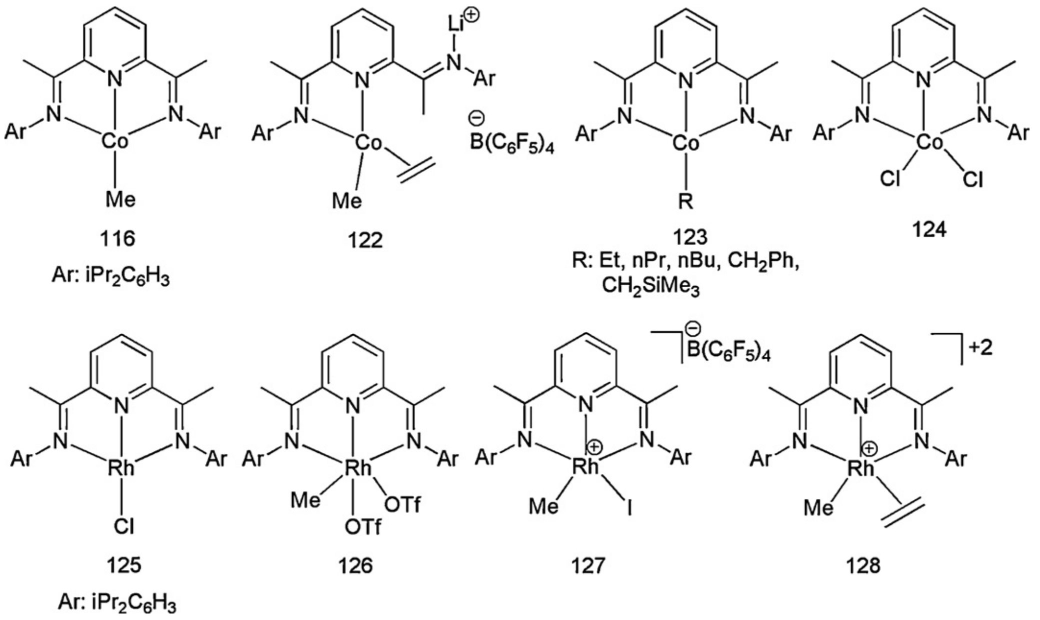
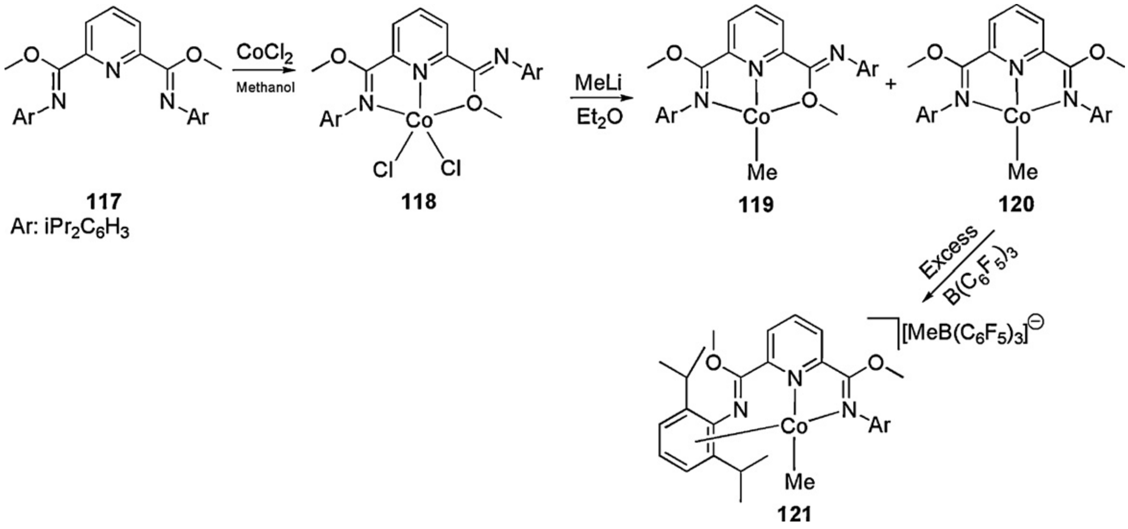


Fig. 17. Group IX non-metallocene organometallic complexes involved in olefin polymerization.

als, alkyl/aryl palladium-based catalysts with pyridine ligands have been studied to a deeper extent than nickel. Nickel(II) catalysts bearing bis(imino) pyridine ligand of type **101** or **124** have been well studied for ethylene, propylene, and norbornene polymerization, which yields a high degree of polymers with different microstructures. Similarly, random co-polymerization of norbornene with butadiene has also been carried out at room temperature, and the catalysts show relatively low activity at higher temperatures [159,160]; however, their alkyl or aryl counterparts were not of more interest.

Gibson et al. [161] investigated the synthesis of two well-defined cationic highly air and moisture-sensitive dimethyl nickel complexes **129** and **130**. These catalysts are synthesized in two steps from the parent dibromide complexes by treatment with methylmagnesium bromide to produce a good yield. Catalysts **129** and **130** possess square planar geometry and be diamagnetic in nature, in contrast to their dibromide precursors. These complex structures were presumed to be isomers with *trans* heterocycle and methyl groups, as observed in palladium analogues [162]. Both single component catalysts **129** and **130 have** proved to be active ethylene polymerization catalysts, although **129** is less active than its MAO-activated counterpart. This is possibly due to the absence of excess MAO to act as a poison scavenger for the more sensitive cationic alkyl system. The polyethylene produced is of slightly lower molecular weight than the polymer produced by its dibromide counterpart. The observation of activity for **130** provides strong support for the co-catalyst interfering with the ligand, leading to catalyst deactivation. These reports observed that the 2-(imino)pyridines containing alkyl or aryl substituents on the 6- position of the pyridine ring lying on the N_2 plane show reduced activities, which can ultimately result in complete catalyst deactivation. An allyl cationic nickel(II) catalyst was patented by Johnson et al. [163], who reported that the catalyst upon activation by MAO produces fairly good activity in ethylene polymerization and generating branched waxy polyolefin materials with predominating methyl branches. The predominant methyl branching in polymers formed by alkyl catalysts of group X metals indicates that the polymerization



Scheme 3. Different mode of coordination in an active organometallic cobalt catalyst.

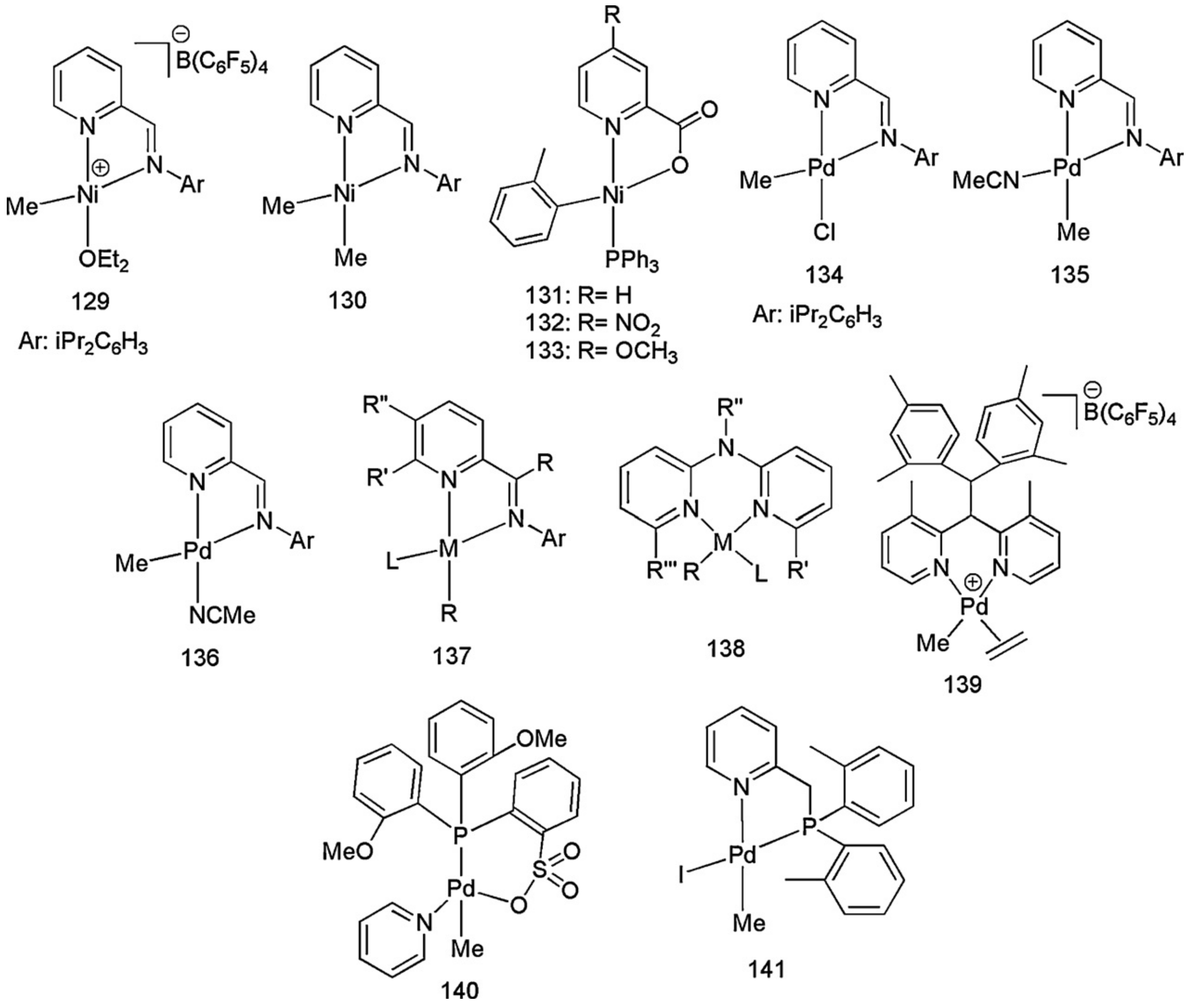


Fig. 18. Group X non-metallocene organometallic catalysts with pyridine scaffold involved in olefin polymerization.

catalysts can isomerize the produced metal alkyls via a chain-walking mechanism as occurs for Ni(II) and Pd(II) diimines. Cavell et al. [164,165] reported three single-component N-O chelated tolylnickel(II) complexes **131**–**133** as ethane polymerization and CO/ethene co-polymerization catalysts. Catalysts **131**–**133** differ only for the substitutions at the 4- position of pyridine-2-carboxylic acid. The catalytic performance of **131**–**133** for ethylene polymerization is strongly dependent on the basicity of the bidentate ligands. Although many aspects of the mechanism remain ambiguous, the change in chain lengths of the products can be explained by the fact that catalysts derived from less basic 4-substituted ligands may follow a different mechanistic pathway than that followed by catalysts derived from a non-substituted ligand. The presence of electron-withdrawing substitution on a pyridine ring (**132**) transforms an oligomerization catalyst into a polymerization catalyst.

Kress et al. reported [166] the oligomerization activity of olefins by a series **134**–**136** of cationic methyl palladium(II) catalysts with 2-(imino)pyridine ligand. The ligand system is prepared by the conventional method of treating 2-acetylpyridine with 2,6-diisopropyl aniline at a 1:1 molar ratio. Catalyst 131 was treated with $NaB\{3,5\text{-}(CF_3)2\text{-}C_6H_3\}_4$ to obtain the analogue cationic complex; however, it produced *cis* and *trans* cationic isomers **135** (major) and **136** (minor), respectively. These catalysts can form higher oligomers, and the results can be reconciled with conventional mechanistic assumptions [167]; i.e., β-hydride transfer from the growing oligomer chains to the palladium catalytic centers is followed either by a reverse but regio-selective different reaction or by displacement of the olefin of the resultant palladium-olefin-hydride complex. Several research groups have described neutral and cationic Ni(II) and Pd(II) complexes with unsymmetrical imino-pyridine ligands of type **137**, which generally produce greatly reduced ethylene polymerization activities and reduced molecular weights [168–171]. The absence of any significant steric protection in catalysts of type **138** leads to the formation of higher α-olefins [172]. Jordan et al. reported that Pd(II) complexes with bispyridyl methane ligand **139** promote dimerization, oligomerization, and polymerization of ethylene depending on the bulkiness of substituents of the ligands [173]. Pd(II) and Ni(II) catalysts using phosphine-sulfonate ligands have attracted recent attention. The catalysis was originally observed by Drent and Pugh [174], who reported a methyl palladium catalyst **140** with pyridine ring suitable for co-polymerization of ethylene with acrylate to produce the polymer-containing acrylate repeating unit in the main chain. P, N donor methyl Pd(II) catalyst **141** has been reported in the literature; **141** was tested for ethylene polymerization in CH_2Cl_2 after activation of the complex with $[NaB(3,5\text{-}CF_3C_6H_3)_4]$ in diethyl ether, which can significantly oligomerize ethylene to a mixture of isomeric olefins. The contents of linear olefins are significantly higher [175].

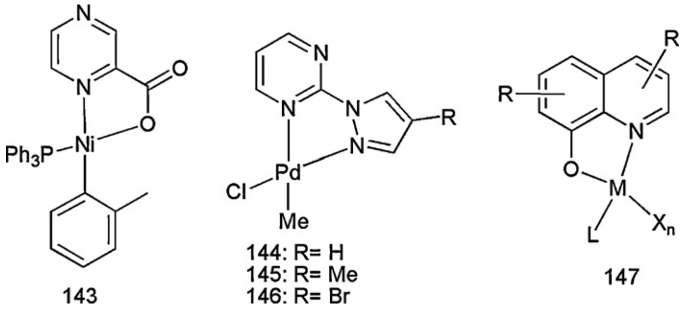


Fig. 19. Pyrazine, pyrimidine, and quinoline-derived olefin polymerization catalysts.

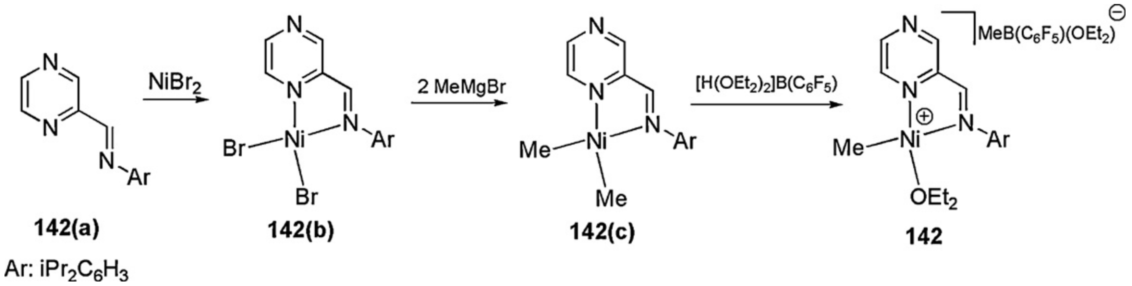
4.2. Pyrazine/pyrimidine-based catalysts

Pyrazine and pyrimidine heterocycles are characterized by six-membered heterocycles with two nitrogen atoms as heteroatoms at the 4- and 3- positions, respectively. Analogous to pyridine-based catalysts, pyrazine and other similar family heterocyclic ligands have attracted a great deal of interest (Fig. 19). The chelation properties of these heterocycles are close to those of pyridine; however, the catalysts based on these heterocycles are rather less in number compared to pyridine. Gibson et al. [161] reported the synthesis of 2-(imino)pyrazine by the conventional reaction between pyrazine-2-carboxaldehyde and 2,6-diisopropyl aniline. A cationic methyl nickel(II) complex **142** was formed from its dimethyl counterpart and studied for ethylene polymerization (Scheme 4). The pyrazine derivative **142** is sterically identical to the active precatalyst of the similar ligand composed of pyridine. Thus, it is surprising that **142** shows no polymerization activity upon activation with MAO. The reduced basicity of the pyrazine nitrogen donor ($pK_a = 0.4$ vs. 5.2 for pyridine) may lead to catalyst deactivation via ligand dissociation. Another possibility is coordination of the remote nitrogen donor of the pyrazine moiety to Lewis-acidic aluminum centers of the co-catalyst, which could also lead to catalyst deactivation. In a similar fashion, Cavell et al. [165] reported the synthesis and catalytic activity of tolylnickel(II) catalyst **143** towards ethylene polymerization. Pyrazine-2-carboxylic acid itself acts as a uninegative ligand; furthermore, tolyl and triphenylphosphene groups are the other two coordination sites that fulfill the tetrahydral geometry of **143**. Catalyst **143** is subjected to ethane polymerization; the product distribution consists of a mixture of oligomers and polyethylene with approximately 55% of the product polyethylene, and the oligomer fraction is highly linear. CO/ethylene co-polymerization yields a product consisting of approximately 70% polyketone, the rest being primarily oligomeric species. Noels et al. [176,177] reported the synthesis of a new series of 2,6-bis(imino)pyrazinyl ligands and their corresponding dichloro iron complexes as efficient ethylene polymerization catalysts; however, their organometallic counterparts have not yet been studied by any other groups.

The 2,6-bis(imino)pyrimidine ligands are readily accessible from 2,4-dibenzoyl-6-methylpyrimidine and the required aniline in the presence of $Si(OEt)_4$ and a catalytic amount of H_2SO_4. Catalytic studies on these systems show them to possess only one-third {dichloro iron(II) catalyst} or one-half {dichloro cobalt(II) catalyst} of the activity of analogous bis(imino)-pyridine systems. Furthermore, the polymer data of the pyrimidine and pyridine-based systems follow almost similar trends. Again, there have been no reports on the synthesis and catalytic performances of organometallic catalysts from these counterparts in olefin polymerization. A series of methyl palladium catalysts **144**–**146** derived from 2-pyrazolyl pyrimidine were reported by Claver et al. [178]. The N-heterocyclic ligands were prepared through the conventional cyclization method by treating appropriate diketones with pyrimidine hydrazide [179,180]. Catalysts **144**–**146** were tested for the CO/4-tert-butylstyrene (TBS) co-polymerization reaction. All three catalysts were active towards 4-tert-butylstyrene/CO co-polymerization, which in all cases led to syndiotactic polyketones. High stereochemical control was observed, which was attributed to chain-end control. This is because of the interaction of the growing chain with the incoming styrene unit, which inserts exclusively in the 2,1 fashion. Similar kinds of interactions were also found with the same monomer units using different catalysts systems [181,182].

Many groups have made multiple attempts to develop active pyrazine or pyrimidine-based non-metallocene organometallic catalysts for olefin polymerization reactions, which have been reported in the form of patents. Xu et al. [183,184] claimed a patent on a highly active magnesium-based supported catalyst component useful in a catalyst system for the co-polymerization of ethylene and other α-olefins. The catalyst system is connected with an alkoxysilane ester and halogen-substituted silane to form an organic silicon complex. Furthermore, it is connected with a transition metal (viz., alkyl titanium) to form an organic silicon complex, which is then contacted with a substituted pyrazine derivative. Finally, the entire compound is contacted with a magnesium-based composite support that was prepared *in situ* by reacting metallic magnesium with an alkyl or aryl halide to form the catalyst component. Pyrazine-based ligands used for the study include 2-pyridine, 2-pyrimidine, and 2-alkylsilane substituted pyrazine derivatives along with alkyl or aryl substitutions at the 3, 5, and 6 positions. For 2-heterocyclic substituted pyrazines, an additional coordination is observed from the heteroatom present at the 2- position.

Schuchardt claimed a patent [185] on a single-site catalyst system useful for the polymerization of olefins. The catalyst system is comprised of an optional activator and complex that incorporates a group III–X transition metal with an alkyl or aryl group and a pyrimidine-based neutral or anionic ligand. Ligand systems with imine substitution at the 2- or 6- positions are easily prepared by the action of aldehyde/ketone with 2- or 6-aminopyrimidine. These complexes preferably form four-membered chelate with pyrimidine and imine nitrogen atoms. Apart from imine ligands,



Scheme 4. Preparation of cationic nickel catalyst with pyrazine scaffold.

Table 2
Polymerization results obtained by selected single-site N-heterocyclic organometallic catalysts containing a six-membered ring system.

M[a]	Cat.	Amount (μmol)	Co-catalyst			Sol[c]	T (°C)	P (atm)	t (min)	Yield (mg)	R_p[d]	$M_w \times 10^{-4}$	M_w/M_n	Ref.
			MAO (equiv)	Trityl[b] (equiv)	$^{i}Bu_3Al$ (equiv)									
E	**50**	4.5	1000	0	0	tol	50	5	30	550	48.8	2.0	2.8	[84]
E	**50**	9.0	0	3	200	tol	50	5	10	3140	418.0	145.0	2.0	[84]
E	**51**	9.0	0	3	200	tol	50	5	5	1970	472.0	6.6	4.2	[84]
E	**52**	9.0	0	3	200	tol	50	5	5	2260	602.0	5.0	4.1	[84]
P[c]	**53**	25.0	1000	0	0	tol	25	5	15	3000	96.0	15.6/0.1[e]	1.3/1.5[e]	[84]
P	**53**	9.0	1000	0	0	tol	25	5	15	1110	98.0	16.3/0.1	1.4/1.5	[84]
P	**53**	9.0	1000	0	0	tol	50	5	15	710	64.0	17.8/0.09	1.2/1.2	[84]
P	**56**	7.0	500	0	0	tol	0	liq.[f]	30	3	0.86[g]	n.r.	n.r.	[85]
P	**58**	3.5	2000	0	0	tol	0	liq.	30	904	520.0[g]	26.2/0.1	2.0/1.6	[85]
P	**58**	3.5	3000	0	0	tol	0	liq.	30	172	980.0[g]	32.1/0.1	2.5/1.5	[85]
P	**58**	3.5	4000	0	0	tol	0	liq.	30	404	230.0[g]	19.0/0.1	1.9/1.4	[85]
E	**60**	0.3	0	2	50	tol	100	7	20	65	4.1[h]	132.0	3.3	88a
E	**61**	0.3	0	2	50	tol	100	7	20	179	12.4[h]	223.0	3.6	88a
E	**62**	0.3	0	2	50	tol	100	7	20	355	22.0[h]	172.0	6.7	88a
E	**63**	0.3	0	2	50	tol	100	7	20	71	3.40[h]	65.0	2.9	88a
E	**64**	0.3	0	2	50	tol	100	7	20	244	12.0[h]	163.0	5.0	88a
E	**65**	0.6	0	2	50	tol	100	7	20	26	0.7[h]	10.0	3.3	88a
E/P[i]	**60**	0.9	0	2	50	tol	100	7	20	42	0.4[j]	17.1	n.r.[k]	88a
E/P[i]	**61**	0.6	0	2	50	tol	100	7	20	26	0.4[j]	89.1	n.r.	88a
E/P[i]	**62**	0.6	0	2	50	tol	100	7	20	137	1.9[j]	[l]-	n.r.	88a
E/P[i]	**64**	0.6	0	2	50	tol	100	7	20	99	1.0[j]	-	n.r.	88a
P	**66**	2.7	0	2	219	tol	25	0.7	5	1000	n.r.	n.r.	n.r.	[90]
P	**66**	0.03	0	0	8[m]	tol	110	6.9	3	n.r.	8282	13.0	2.0	[90]
Nb	**83**	2.0	–[n]	–	–	bz	80	-	30	10	55.0[o]	n.r.	n.r.	[115]
Nb	**84**	2.0	–[n]	–	–	bz	80	-	30	6	32.0[o]	n.r.	n.r.	[115]
E	**86**	0.5	0	0	0	n.r.	80	6.5	240	n.r.	0.69	3.6	1.8	[120]
E	**87**	20.0	5000	0	0	tol	r.t.	1	30	n.r.	1394	oligom.[p]	-	[127]
E	**88**	20.0	5000	0	0	tol	r.t.	1	30	n.r.	5490	oligom.[q]	n.r.	[127]
E	**89**	20.0	5000	0	0	tol	r.t.	1	30	n.r.	73.0	n.r.	n.r.	[127]
E	**111**	4.0	1000	0	0	tol	30	5	20	3680	550.0	1.0	2.2	[143]
E	**116**	90.0	0	1	0	tol	r.t.	2	30	1400	16.0	n.r.	n.r.	[150]
E	**118**	9.3	1000[r]	0	0	tol	r.t.	6.7	20	n.r.	5.96	0.08	1.3	[150]
E	**119**	9.3	1000	0	0	tol	r.t.	6.7	20	n.r.	7.30	2.9	2.3	[150]
E	**124**	0.5	1000	0	0	tol	n.r.	6.9	15	884	1010	2.1	3.4	[155]
E	**129**	10.0	0	0	0	mc	0	1	60	1100	110.0	0.04	1.7	[161]
E	**139**	30.0	0	0	0	mc	25	3	1080	2290	n.r.	2.3	1.9	[173]
E	**139**	30.0	0	0	0	cbz	25	3	1080	2250	n.r.	3.5	1.9	[173]
E	**142(b)**	10.0	200	0	0	tol	25	1	30	trace	< 1.0	n.r.	n.r.	[161]
E	**142**	10.0	0	0	0	mc	0	1	60	600	60.0	0.2	2.1	[161]

[a] Type of monomer: E—ethylene, P—propylene, and Nb—norbornene.

[b] Trityl: $[Ph_3C][B(C_6F_5)_4]$.

[c] Type of solvent: tol: toluene, bz: benzene, mc: methylene chloride, and cbz: chlorobenzene.

[d] Rate of polymerization in kg-polymer $mol^{-1}\ h^{-1}\ atm^{-1}$.

[e] Two values in these columns due to bimodal distribution.

[f] Bulk polymerization in liquefied propylene.

[g] R_p in kg-polymer $mol^{-1}\ h^{-1}$.

[h] R_p in (kg-polymer)$(mmol)^{-1}\ h^{-1}$(mol/L ethylene)$^{-1}$.

[i] E/P co-polymerizations were performed in 5 mL of toluene at 1 atm of propylene pressure out of 7 atm total pressure.

[j] R_p in (kg-polymer)$(mmol)^{-1}\ h^{-1}$.

[k] Not reported.

[l] Multimodal distribution.

[m] With $^{i}Bu_2AlH$.

[n] Norbornene polymerizations in the presence of PMe3 ([P]/[V] = 3).

[o] Turnover number in mmol of norbornene consumed per mmol of vanadium.

[p] Schultz-Flory distribution with K value of 0.46 and 92% of α-olefins.

[q] Schultz-Flory distribution with K value of 0.78 and 89% of α-olefins.

[r] MAO/BF_3 complex.

2-methoxy and 2-hydroxy pyrimidines are also treated as ligands for the preparation of active olefin polymerization catalysts.

4.3. Benzo-fused six-membered heterocyclic catalysts

Olefin polymerization catalysts encompassing benzo-fused six-membered heterocycles as core N-heterocyclic donor ligands have gained much interest in current research. Among the series of these heterocyclic cores, quinoline-derived non-metallocene catalysts are showing promise. A few 2-substituted quinazoline and quinoxaline-derived catalysts have also been reported; however, their organometallic counterparts have not been found. In addition to these two classes, phthalazine-derived catalysts can also polymerize olefins to the desired compositions; however, these derivatives form active bimetallic catalyst systems by involving their diazine fragment as an endogenous bridging module.

Quinoline-based chromium(III) catalyst was tested for the polymerization of propylene. The ligand system has a Cp substitution at the 8- position of the quinoline and can polymerize propylene to an atactic polymer with moderate activity [186]. 2-Substituted quinoline ligands were prepared by the action of quinoline-2-carboxaldehyde on aldehyde/ketone. These ligand systems can form stable five-membered chelate complexes by involving its heterocyclic and imine nitrogen atoms in the coordination. Group III–X metals with alkyl/aryl substitutions were reported by Haddleton [187]. His invention is related to a process for the atom transfer polymerization of olefinically unsaturated monomers in which molecular weight control is achieved by the presence of transition metals. The substitutions on aldehyde/ketone used for the preparation of ligand systems are C1–C20 alkyls, hydroxyalkyl, or carboxyalkyl—particularly C1–C4 alkyl, such as methyl or ethyl—*n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *tert*-butyl, cyclohexyl, 2-ethylhexyl, octyl, decyl, or lauryl. The activity is high for methyl. These catalysts unexpectedly work at a wide variety of temperatures, including room temperature and as low as −15 °C. Accordingly, the catalyst is preferable used at a temperature of −20 to 200 °C, especially −20 to 150 and 20 to 130 °C. The olefinically unsaturated monomer may be methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate and the corresponding acrylate, fictionalized methacrylates, styrene, methacrylonitrile, or a diene such as butadiene. Another important report [188] was made by the same author in relation to supported quinoline based ligands and their organometallic catalysts for the use in the polymerization of olefinically unsaturated monomers such as vinylic monomers, where a compound is attached to support. Nagy et al. claimed a patent [189] for their remarkable invention in the preparation of non-metallocene organometallic titanium, zirconium, and halfnium catalysts with bidentate quinoline ligands. The catalysts of the general formula **147**, where X is independently selected from C1–C6 alkyls or C1–C6 alkoxy or alkyl cyclopenatdienyl derivatives, and R is independently selected from the abovementioned substituents. These catalysts are efficient ethylene polymerization catalysts with good activities.

4.4. Summary of polymerization results obtained by N-heterocyclic organometallic catalysts of six-membered ring system

To help the reader to categorize the large array of polymerization catalysts presented in this section, a summary of polymerization results obtained by selected N-heterocyclic organometallic catalysts of six-membered ring system discussed is given in Table 2. This table should be used as an indicator of activity trends, rather than an absolute measure of catalyst performance, since the activities are subject to polymerization conditions that may not have been optimized. Taking a careful review of the polymerization results, the field of olefin polymerization catalysis has developed dramatically over the past ten years or so, with some of the most significant recent advances occurring for late transition metal systems. The discovery of a highly active family of catalysts based on iron, cobalt, nickel and palladium has highlighted the possibilities for further new catalyst discoveries. The development of catalyst discovery is likely to be limited only by the talent and scientific passion of the synthetic organometallic and coordination chemist for ligand design, since a systematic design of ligand structure considering the steric protection of active sites plays a crucial part in the achievement of highly active catalyst producing high molecular weight polymers.

5. Conclusions

This review article explains many aspects regarding the coordination mode, structure, and catalytic facets of single-site non-metallocene catalysts with N-heterocyclic scaffolds employed in olefin oligo/polymerization. Research activities based around non-metallocene single-site catalysts bearing N-heterocyclic ligand frameworks have resulted in a wealth of new chemistry over the past several years. Following the initial discovery of highly active late first row transition metal complexes as efficient catalysts for olefin polymerization, many N-heterocyclic ligand frames supported for group III–X metals have also been identified as compatible ligands for the preparation of the desired catalyst for catalytic polymerization applications. Furthermore, these discoveries have gained much attention in getting desired oligomeric/polymeric products. Alkylation/alkylsilylation to the dihalo metal catalysts with N-heterocyclic scaffolds has now been identified as the major method for obtaining non-metallocene organometallic metal pre-catalysts; presently, this is being explored for obtaining title compounds. The ability of the N-heterocyclic ligand framework with definite electronic and steric modulations to support metals, especially first row transition metals atoms, in different oxidation states has been observed, and it is thought to be important for obtaining the desired polymeric product. Indeed, there is evidence that non-metallocene organometallic compounds act significantly in order to obtain high molecular weight polymers as metallocene-based catalysts. An important attempt has been made for alkyl/aryl cobalt(II)/iron(II) catalysts with bis-(imino)pyridine ligands to be reduced to a cobalt(I)/iron(I) species upon addition of aluminum co-catalysts.

One of the most significant advances in understanding the factors responsible for stabilizing active catalysts during polymerization is the alkyl metal complex; hence, the recognition of alkyl substituents with metal ions can play a crucial role in not only stabilizing the active site but also controlling the chain-transfer processes in polymerization. Based on this inference, many of the alkyl/aryl metal catalysts have been reported as efficient olefin polymerization catalysts even in the absence of aluminum co-catalysts, and this property of the alkyl/aryl metal catalysts is well explained in this review.

Acknowledgments

This work was supported by grants-in-aid for the World Class University Program (No. R32-2008-000-10174-0) and the National Core Research Center Program from MEST (No. R15-2006-022-01001-0).

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