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Advances in Non-Metallocene Olefin Polymerization Catalysis

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Contents

I. Introduction and Development of the Field 283
II. Scope of Review 284
III. Group 3 Catalysts 286
IV. Group 4 Catalysts 286
  A. Cp and Other Carbon-Donor Ligands 286
    1. Cp-Based Precatalysts with an Additional Neutral Donor 286
    2. Cp-Based Precatalysts with an Additional Anionic Donor 286
    3. Metallocene-Related Precatalysts 288
    4. Non-Cp Carbon-Based Ligands 289
  B. Chelating Amides and Related Ligands 289
    1. Diamide Ligands 289
    2. Diamide Ligands with an Additional Donor 290
    3. β-Diketiminates and Related Six-Membered Chelate Ligands 291
    4. Iminopyrrolides and Related Five-Membered Chelate Ligands 291
    5. Amidinates and Related Four-Membered Chelate Ligands 292
    6. Amide Ligands Forming Three-Membered Chelates 293
  C. Chelating Alkoxides, Aryloxides, and Related Ligands 293
    1. Salicylaldiminato Ligands 293
    2. Bis(phenoxy) Amine Ligands 294
    3. Other Aryloxide, Alkoxide, and Thiolate Ligands 294
    4. Aryloxide and Alkoxide Ligands in Combination with Cp 294
V. Group 5 Catalysts 295
  A. Precatalysts in the +V Oxidation State 295
  B. Precatalysts in the +IV Oxidation State 296
  C. Precatalysts in the +III Oxidation State 296
VI. Group 6 Catalysts 297
  A. Cp-Based Ligands 297
  B. Non-Cp-Based Amide, Amine, and Phenoxy Ligands 298
VII. Group 7 Catalysts 300
VIII. Group 8 Catalysts 300
  A. Neutral Bis(imino)pyridine and Related Ligands 300
  B. Anionic Ligands 302
IX. Group 9 Catalysts 302
X. Group 10 Catalysts 303
  A. Neutral Ligands 303
    1. α-Diimine and Related Ligands 303
    2. Other Neutral Nitrogen-Based Ligands 304
    3. Chelating Phosphorus-Based Ligands 304
  B. Monoanionic Ligands 305
    1. [PO] Chelates 305
    2. [NO] Chelates 306
    3. Other Monoanionic Ligands 306
    4. Carbon-Based Ligands 306
XI. Group 11 Catalysts 307
XII. Group 12 Catalysts 307
XIII. Group 13 Catalysts 307
XIV. Summary and Outlook 308
XV. Glossary 308
XVI. References 308

I. Introduction and Development of the Field

The field of olefin polymerization catalysis has experienced a phenomenal acceleration in research activity over the past 5 years, with many academic and industrial research laboratories engaging in the design of coordination and/or organometallic precatalysts for the controlled synthesis of polyolefin products. The seeds of this activity are traceable to advances in Group 4 metallocene systems and their related half-sandwich titanium amide (“constrained geometry”) catalysts during the 1980s.[1] During that period, studies on the Group 4 metallocenes afforded much needed insight into the nature of the activated species, and the possibilities for controlling the nature of the polyolefin products were most elegantly demonstrated by the capacity of *ansa*-metallocene structures to polymerize propylene with high iso- or syndiotactic control.[2] Changes to the ligand skeleton provided access to more unusual materials, such as hemi-isotactic polypropylene (PP) and stereo-block (isotactic−atactic) materials.[3] Contemporaneously, the half-sandwich titanium amide system, often also referred to as a “metallocene” system, was shown to possess an unparalleled capacity to incorporate longer chain α-olefin comonomers with the same degree of incorporation over the entire molecular weight range of the polyolefin product.[1]

During the first half of the 1990s, interest grew in developing new generation “non-metallocene” catalysts, partly to avoid the growing patent minefield in Group 4 cyclopentadienyl systems, but also to

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Vernon Gibson was born in Grantham, England, in 1958. He received his B.Sc. degree from the University of Sheffield in 1980, and his D.Phil. degree from the University of Oxford in 1984, with Malcolm Green. He was a NATO postdoctoral fellow with John Bercaw at Caltech from 1984 to 1986, before being appointed to a lectureship in Inorganic Chemistry at the University of Durham, England. He was promoted to Full Professor at Durham in 1992, and in 1995 moved to Imperial College, where he now holds the Sir Edward Frankland BP Chair of Inorganic Chemistry. His research interests include fundamental aspects of metal coordination and organometallic chemistry, and applications of discrete metal complexes in polymer synthesis.

Stefan Spitzmesser, born in Bühl, Germany, began studying Chemistry in 1991 at the University of Konstanz in Germany. During his studies, he also spent one year as an undergraduate research assistant with K. P. C. Vollhardt at the University of California, Berkeley. In 1997, he graduated from Konstanz with a diploma thesis on *ansa*-zirconocenes under the direction of H.-H. Brintzinger. After a brief spell as a business consultant, he joined the group of V. C. Gibson at Imperial College in London in 1998. He was recently awarded a Ph.D. for his work on the development of new non-metallocene olefin polymerization catalysts.

harness the potential of other metals to polymerize ethylene on its own and with other olefinic monomers. It was a discovery in the mid-1990s that was to have a galvanizing effect on researchers in the polyolefin catalysis field. Although some earlier work on nickel catalyst systems of the type employed in the Shell Higher Olefin Process (SHOP) had revealed the potential for late transition metals to polymerize ethylene,[4−7] it was the discovery of highly active (α-diimine)nickel catalysts capable of polymerizing ethylene to either linear or highly branched polyethylene (PE), depending on the ligand backbone and reaction conditions, that dramatically demonstrated the possibilities for expanding the commercially useful metals beyond the first half of the transition series.[8] Due to their enhanced functional group tolerance, such late transition metal systems also offered the commercially attractive possibility of being able to incorporate polar comonomers into polyolefin materials, to give modified surface properties at low levels of comonomer incorporation, to change the bulk properties of the polyolefin at higher levels of incorporation, or to provide a low-temperature/pressure route to existing materials such as ethylene−vinyl acetate (EVA) copolymer. Moreover, the recognition that well-defined nickel catalysts contain a coordinatively unsaturated cationic metal alkyl as the active site allowed a direct relationship to be drawn between the well-established early transition metal and the "newcomer" late transition metal systems. This relationship could clearly be built upon to explore uncharted areas of the transition series and, more generally, the periodic table. The potential for this approach was soon to be realized with the discovery in the late 1990s of highly active ethylene polymerization catalysts based on iron, a metal with no previous track record in olefin polymerization.[9,10]

Another significant development over the past 5 years or so has been the introduction of systems capable of catalyzing the living polymerization of olefinic monomers.[11] The absence of chain-transfer or chain-termination processes allows access to polyolefinic materials with very narrow molecular weight distributions (typically <1.1), block copolymers, and polymers with novel topologies.

II. Scope of Review

In 1999, we published a review of the main developments in "non-metallocene" polymerization catalysis covering the period up to mid-1998.[12] The area has gained such rapid momentum, with many new catalyst systems being reported across and also beyond the transition series, that a further review of the field seemed appropriate. Figure 1a shows the increase in the number of publications by year over the past decade, while Figure 1b gives the number of publications by Group for the 4-year periods 1994−1997 and 1998−2001. Notable are the increased number of publications for the Group 8 and Group 10 metals over the past 4 years, with the number of publications on the Group 10 metals for the period 1998−2001 substantially surpassing those for the Group 4 metals over the previous 4-year period. This review highlights key further developments in the design and applications of new "non-metallocene" catalyst systems that have been reported since 1998. Included are half-sandwich Group 4 metal systems with "constrained geometry" type ligands, often misdesignated as "metallocenes" in the early olefin polymerization catalysis literature. Advances reviewed previously will not be included, unless there have been major developments in the catalyst or products.

All catalysts have been classified according to the transition metal group and the ligand-donor set involved. However, it has to be borne in mind that structures shown in this review generally depict the precatalysts, which need a suitable activator to form a catalytically active species.[13] Unless stated otherwise, excess methylaluminoxane (MAO) has been

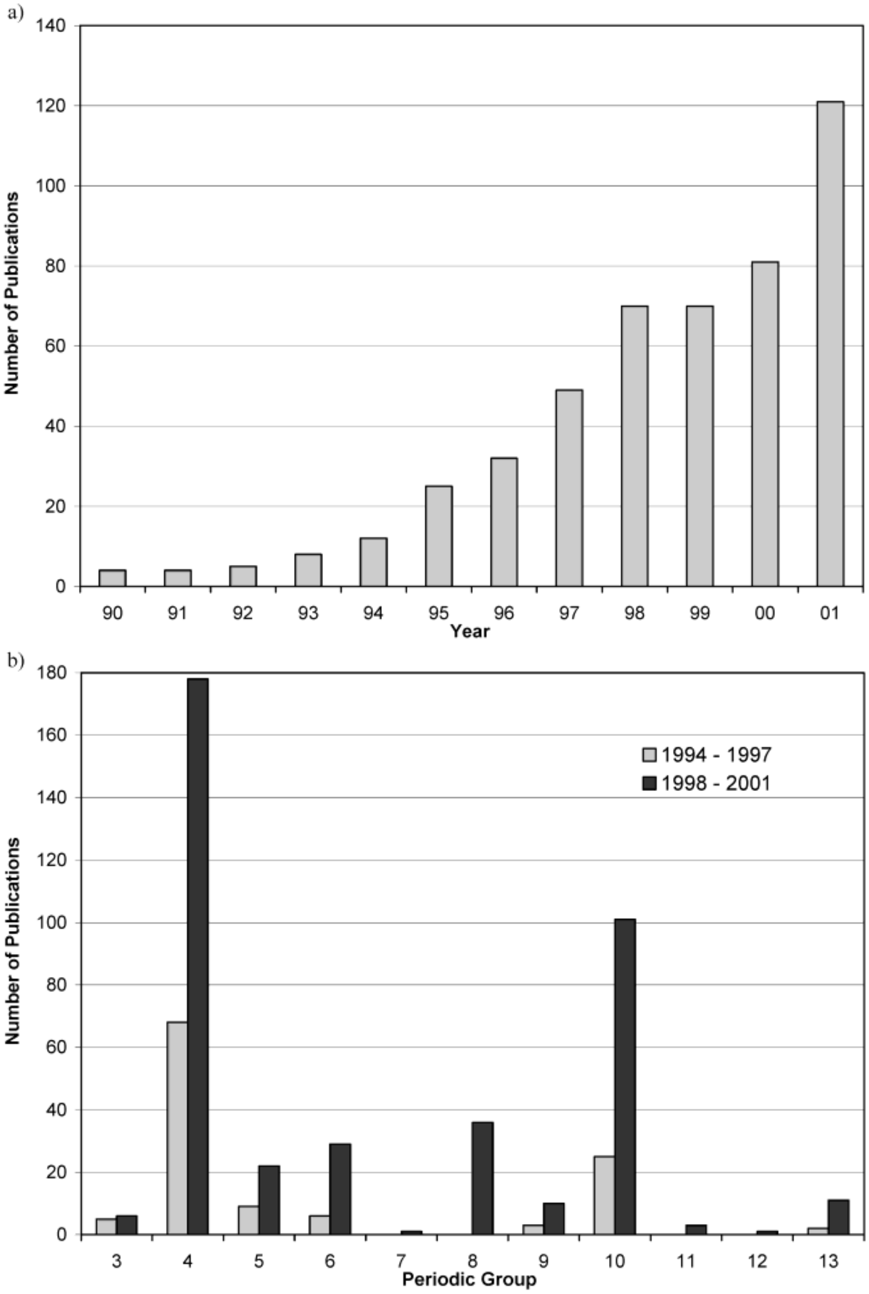


Figure 1. Numbers of publications on non-metallocene olefin polymerization catalyst systems appearing in the academic literature: (a) by year between 1990 and 2001, and (b) by periodic group for the 4-year periods 1994−1997 and 1998−2001. Source: References found in Britovsek et al.,[12] Ittel et al.,[386] and this review.

employed as cocatalyst. For many catalysts of Group 10 metals, cationic alkyl, aryl, and allyl derivatives have been isolated that do not require any cocatalysts and are then referred to as “single-component” catalysts. In recent years, modified MAO (MMAO), prepared by the controlled hydrolysis of a mixture of trimethylaluminum (TMA) and triisobutylaluminum, has emerged as an alternative activator. Advantages of MMAO include its improved solubility in aliphatic solvents and enhanced solution storage stability.[14]

Catalyst activities have been converted, where necessary, into the units g mmol^{-1} h^{-1} bar^{-1} for gaseous monomers, such as ethylene, and g mmol^{-1} h^{-1} for reactions carried out in liquid α-olefins, such as 1-hexene. These conversions were made irrespective of the dependency of the polymerization rate of a catalyst on monomer concentration (pressure) in order to obtain comparable activity numbers. They are classified as described previously, i.e., very high (>1000), high (1000−100), moderate (100−10), low (10−1), and very low (<1).[12] However, when comparing reported activities, it should be borne in mind that they are often strongly influenced by several variable and interdependent factors, including vessel size, quality of stirring, type of solvent, nature of cocatalysts and scavengers (including the extent of aging of MAO), and the order of reactant addition, as well as the reaction parameters temperature, pressure, and time. In addition, expressing activities in the units g mmol^{-1} h^{-1} bar^{-1} can lead to artificially high values when very short reaction times are extrapolated to 1 h. Many catalysts show very high initial activities followed by rapid deactivation, and, while for certain polymerization processes such as those carried out in solution, very short lifetimes may be acceptable, much longer lifetimes are generally required for gas-phase polymerization. A useful way to reconcile these disparate approaches is to monitor ethylene uptake over the duration of an extended run (e.g., over a period of 1 h) and provide a kinetic profile of the catalyst's performance over this period. Including benchmarking data for existing catalysts with well-established performance characteristics, e.g., metallocenes, (α-diimine)nickel, or [bis(imino)pyridine]iron, can also be very helpful in evaluating the performance of new catalyst systems. It has to be recognized, however, that since conditions giving rise to optimal catalyst performance may differ markedly from catalyst to catalyst, there is no single set of screening conditions that will be appropriate for all new catalysts. Standardization of catalyst test results is therefore problematic, and a significant degree of technical judgment has to be applied in deciding upon a catalyst's suitability to a particular process or product.

III. Group 3 Catalysts

Group 3 catalysts remain a relatively unexplored part of the transition series in the context of olefin polymerization. Utilizing the familiar bridged Cp-amide "constrained geometry" ligand system, Okuda and co-workers prepared the yttrium complexes **1** and **2** (Figure 2), which show very low activities for the polymerization of ethylene in the absence of a cocatalyst.[15] Both complexes, however, also polymerize polar monomers such as *tert*-butyl acrylate and acrylonitrile, albeit by different mechanisms, whereby initiation rate and polymer yield are lower for the dihydride complex **2**. In both cases, and for both monomers, atactic polymer is produced.[16]

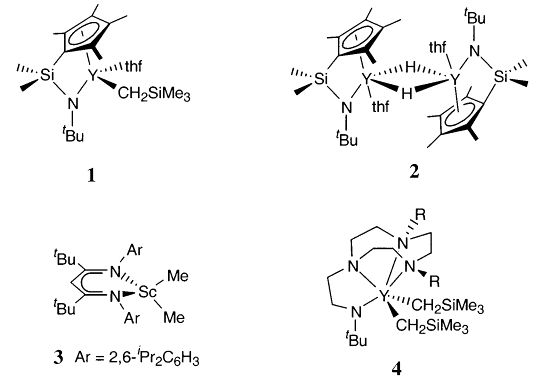


Figure 2. Group 3 metal precatalysts.

The β-diketiminate complex **3**, reported by Piers and co-workers, is moderately active for the polymerization of ethylene. It also proved possible to isolate and structurally characterize the cationic methyl derivative [(β-diketiminate)ScMe][MeB(C_6F_5)$_3$].[17,18] Hessen and co-workers[19] have developed a new ligand system based on 1,4,7-triazacyclononane with a pendant amide donor. Upon reaction of the yttrium complex **4** with [HNMe$_2$Ph][B(C_6F_5)$_4$], they were able to prepare a cationic alkyl derivative which afforded high-molecular-weight PE with an activity of up to 1790 g mmol^{-1} h^{-1} bar^{-1}.

IV. Group 4 Catalysts

A. Cp and Other Carbon-Donor Ligands

1. Cp-Based Precatalysts with an Additional Neutral Donor

Mono(cyclopentadienyl) Zr and Ti complexes with piano-stool structures are generally found to exhibit lower olefin polymerization activities than their bis-Cp metallocene analogues.[20−22] Inclusion of a pendant neutral donor such as NMe$_2$, as shown in complexes of type **5** (Figure 3), affords increased activities of up to 2500 g mmol^{-1} h^{-1} bar^{-1} (**5a**, R = H, X = Cl).[23] The pendant donor is generally coordinated to the metal center as seen in **5a**; however, nonassociation of the donor as in **5b** can also be obtained, depending on the nature of the Cp ligand and the metal substituents X. In both cases, increased air and temperature sensitivity, relative to that of the simple half-sandwich complexes, is observed.[24] Substitution of the pendant amino donor in **5** by an ethylene-bridged ether functionality affords only moderately active Ti and Zr catalysts.[25,26]

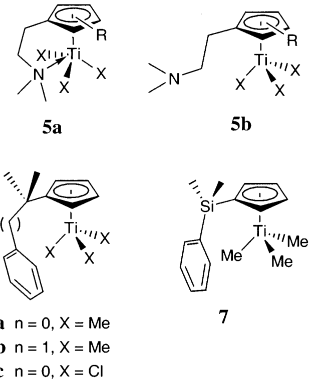


Figure 3. Cp-based ligands with an additional neutral donor.

No coordination of the pendant donor to the neutral metal center is observed for complexes **6** and **7**. Bochmann and co-workers showed that coordination of the pendant phenyl group in **6a** and **6b** occurs only after formation of the cationic species by methyl abstraction with a suitable Lewis acid.[27] The resulting four-coordinate, cationic Ti dialkyl complexes polymerize propylene to atactic polymer with an activity an order of magnitude lower than that for Cp*TiMe$_3$ under similar conditions. The related complex **6c** shows high activity and a remarkable selectivity for the conversion of ethylene to 1-hexene (>87 wt %) after activation with MAO.[28] The pendant phenyl group appears to play a pivotal role in achieving the selectivity. A low-valent Ti species stabilized by coordination of the phenyl group is proposed to be the active species in the catalytic cycle.

2. Cp-Based Precatalysts with an Additional Anionic Donor

The linked Ti $\eta^5\!:\!\eta^1$-Cp-amide complexes **8** (Figure 4) are among the few examples of commercially

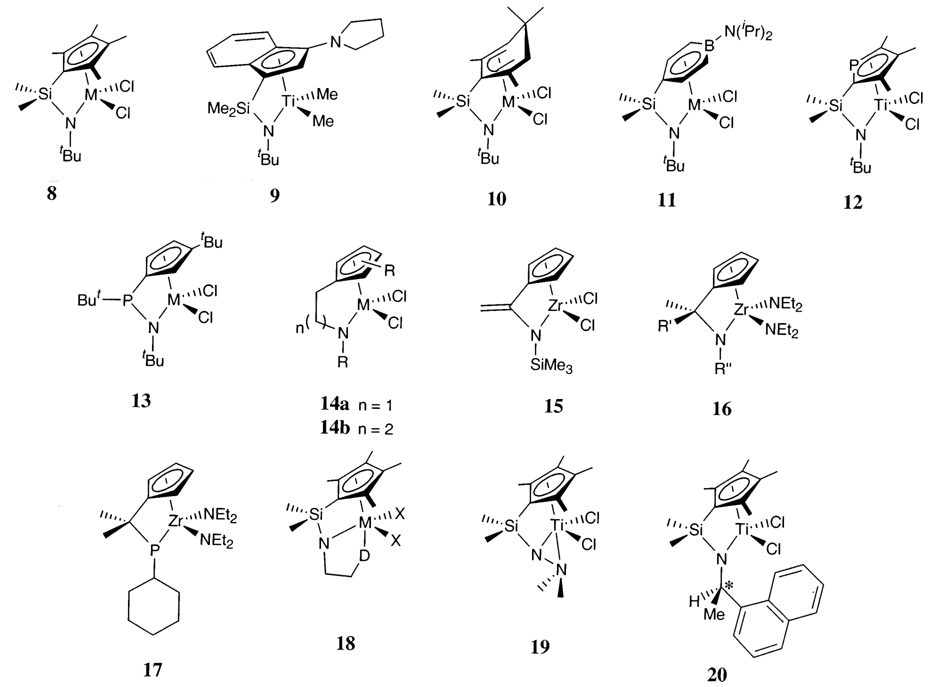


Figure 4. Cp-based precatalysts with an additional anionic donor.

exploited "non-metallocene" catalysts, especially for the copolymerization of ethylene with higher α-olefins. Many new developments on this so-called "constrained geometry catalyst" (CGC) system have been reported in the patent literature[29−40] and were reviewed in 1998 by McKnight and Waymouth.[1] Some structural variations and applications in polymerization reactions have recently been reported in the academic literature. The polymerization of propylene using **8** with different cocatalysts[41] and the copolymerization of ethylene with α,ω-dienes and α,ω-functionalized olefins such as 10-undecen-1-ol have been described.[42,43] In the latter case, the functional group of the comonomer is masked by treatment with Me_3Al, and up to 7 mol % comonomer incorporation can be achieved while maintaining high catalyst activity.

Fluorenyl- and indenyl-based CGCs have also been reported as highly active catalysts for the polymerization of ethylene[44−48] and propylene.[49] The heteroatom-substituted complex **9**, activated with $B(C_6F_5)_3$, shows a dramatic increase in activity for ethylene/1-octene copolymerization. The copolymer has a higher molecular weight than the material derived from the dimethyl derivative of **8**. Both activity and molecular weight of the polymer are strongly dependent on the position of the substituent on the Cp ring.[50] Klosin and co-workers replaced the Cp moiety with the isoelectronic η^5-cyclohexadienyl fragment (**10**) and obtained highly active catalysts for the copolymerization of ethylene and 1-octene, the Zr complexes being slightly more active than their Ti counterparts.[51,52] Other monoanionic, Cp-related moieties such as boratabenzene and phospholyl have previously been shown to give highly active bis-ligand catalysts for the Group 4 metals.[12] More recently, Ashe and co-workers prepared the bridged boratabenzene-amido Ti and Zr complexes of the type **11** and reported high activity for the copolymerization of ethylene with 1-octene. However, the activity and degree of comonomer incorporation (1 mol %) are much lower than those for **8**, which is attributed to increased crowding at the active site afforded by the diisopropylamino substituent.[53] No copolymerization data were reported for the bridged phospholyl-amido complex **12**, but ethylene polymerization activity under high-pressure conditions is very high and comparable to that of **8**. By contrast to **8**, lower molecular weight PE is obtained.[54]

The presence of the bridging unit and the resulting steric constraint imposed in **8** is generally considered to influence the catalytic performance of Cp-amido catalysts, as illustrated by the lower ethylene polymerization activity of the unbridged precatalysts $Cp^*Ti(NMe_2)Cl_2$[55] and $Cp^*Ti[N(SiMe_3)2,6\text{-}Me_2C_6H_3]Cl_2$.[56] However, experimental and computational studies by Erker and co-workers suggest that this influence may not be essential for high activity.[57]

A number of variations on the dimethylsilyl bridging unit in CGCs have been reported. The phosphorus-bridged Cp-amide Ti complex **13** produces linear, high-molecular-weight PE with an activity of 100 g $mmol^{-1}$ h^{-1} bar^{-1}.[58] The related Group 4 complexes, bearing an unbridged diethylamino(^{t}Bu-phosphanyl)-Cp ligand, are only moderately active.[58] In addition to the ethylene-bridged complex **14a**[59] and its propylene-bridged analogue **14b**[60] reported previously,[12] Erker and co-workers synthesized the C_1-bridged complexes **15**[61] and **16**.[62,63] Both **15** and **16** show similar activities in the homopolymerization and copolymerization of ethylene to the related dimethylsilyl-bridged Zr complexes of the type **8**. A 10-fold increase in activity is observed for **17**, bearing a C_1-bridged Cp-phosphide ligand.[62] Further variations of the amido-donor group have been developed by Okuda and co-workers, who have introduced an additional donor unit (**18**) such as D = NMe_2, OMe, or SMe. This leads generally to a decrease in activity for the polymerization of ethylene.[64,65] Lower activities are obtained for the bridged Cp-hydrazido complex **19**, in which the hydrazido functionality can bind in a η^1 or η^2 fashion.[66] Fink and co-workers introduced aromatic substituents on the amido nitrogen donors (**20**) and were able to induce some stereocontrol in the polymerization of propylene, with [mmmm] pentad values for isotactic PP reaching 56%.[67] It is noteworthy that stereocontrol is not a result of the chiral nature of the amido substituent but is caused by interaction of the aromatic ring with the metal center in the active species. Atactic PP is obtained with C_1- and C_s-symmetrical CGCs bearing 2,6-$Me_2C_6H_3$ amido substituents.[68] A (trimethoxy)silane-functionalized Cp-amido catalyst has been prepared by Eisen and co-workers,[69] where the silane functionality is utilized as a covalent anchor for attaching the catalyst to a silica support.

3. Metallocene-Related Precatalysts

There has been much attention directed toward the development of pseudotetrahedral precatalysts bearing ligands with steric and electronic properties related to those of Cp. The coordination chemistry of Group 4 metal complexes based on substituted boratabenzene ligands is well established,[70] and high ethylene polymerization activities have previously been reported for unbridged complexes based on amino-boratabenzene ligands, as represented by **21a** (Figure 5).[71] An increased rate of β-hydrogen transfer is observed for sterically less demanding boratabenzene ligands, for example with R = Ph (**21b**)[72,73] and R = OEt (**21c**),[74−76] resulting in the formation of α-olefins. Ashe et al. have prepared the *ansa*-boratabenzene complexes **22** and the mixed-donor complex **23**. Their activity for the copolymerization of ethylene with 1-octene is high and decreases in the order **23** > **22b** > **22a**, corresponding to an increase in steric congestion about the metal center.[77] Other metallocene-related complexes with monoanionic heterocyclic ligands, e.g., those based on borrolides[78] and thioborrolides,[79] have been reported to give high and moderate ethylene polymerization activities, respectively. Bergman and co-workers utilized the tropidinyl ligand in complexes **24** and **25**.[22] Although lower symmetry than Cp, with its split $2\sigma,4\pi$-electron-donor set, the tropidinyl ligand has been viewed as being isoelectronic to Cp, with a comparable steric influence.[22] Ethylene polymerization activities for the Zr complex **25** are very high and compare favorably to those of Cp_2ZrCl_2 under similar conditions. The analogous Ti complex, as well as the Zr complex **24**, afford low activities. Both the Zr and Ti derivatives of **25** polymerize propylene with moderate activities to give low-molecular-weight PP. The monoanionic hydrido(trispyrazolyl)borate ligand can also be viewed as a Cp mimic, donating six electrons to the metal center through its 6σ-donor set. Several Ti and Zr complexes bearing this ligand have been reported by Nakazawa et al., the highest ethylene polymerization activity being obtained for the mixed-ligand Zr complex **26**.[80] With sterically more demanding mesityl-substituted (trispyrazolyl)borate ligands L, complexes of the type $LMCl_3$ (M = Ti, Zr) are obtained. Their activities, of typically several thousand g mmol^{-1} h^{-1} bar^{-1} for the polymerization of ethylene, are considerably higher than those for **26**;[81,82] the copolymerization of ethylene and 1-hexene has also been investigated.[83] For the related [(bispyrazolyl)acetate}$TiCl_3$ complexes, ethylene polymerization activities of up to 760 g mmol^{-1} h^{-1} bar^{-1} have been reported.[84]

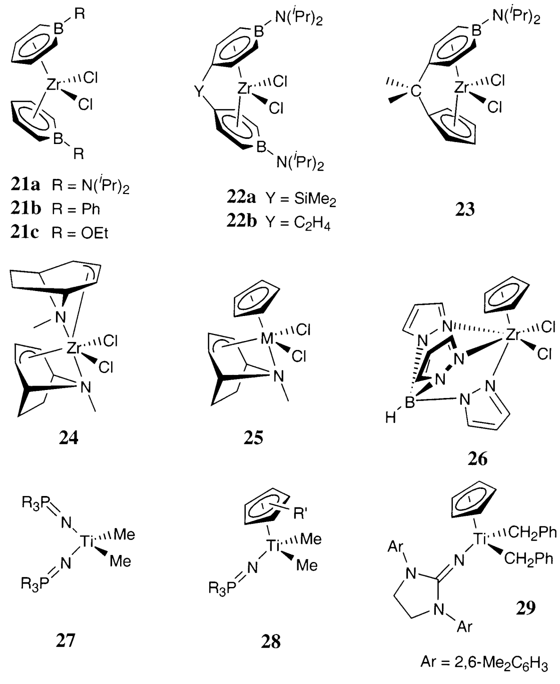


Figure 5. Metallocene-related precatalysts.

Very high activities for ethylene polymerization have been reported by Stephan and co-workers for the Ti complexes **27** and **28**, bearing phosphinimide ligands.[85,86] The conical nature of the phosphinimides approximates the steric bulk of a Cp ligand, but the steric influence lies at greater distance from the metal center.[87] X-ray analysis of a variety of complexes supports the presence of Ti−N multiple bonds through additional π-interactions, thus approximating the Cp ligand also in terms of its electron-donor properties.[88,89] Activities of up to 1160 g mmol^{-1} h^{-1} bar^{-1} are reported for the polymerization of ethylene using the precatalyst **27** (R = ^{t}Bu) when activated with $[CPh_3][B(C_6F_5)_4]$. Similar activities are observed for the related mixed-ligand complexes of the type **28**. Interestingly, activation of **27** (R = ^{t}Bu) with $B(C_6F_5)_3$ affords only moderate activities due to catalyst deactivation processes. The related Zr complexes also show a greatly reduced activity for the polymerization of ethylene.[90] Complexes of the type **27** and **28** also produce low-molecular-weight poly(1-hexene).[87] A related mixed-ligand binuclear Ti phosphinimide complex has been reported by Bochmann and co-workers, but its ethylene polymerization activity is low.[91] Another novel ligand design is shown in **29**, where a similarly strong π-donating ligand is employed. Using this mixed Cp-η^1-guanidinate-type Ti complex, with $B(C_6F_5)_3$ activator, ethylene polymerization activities of up to 1600 g mmol^{-1} h^{-1} bar^{-1} have been achieved.[92] It is also highly active

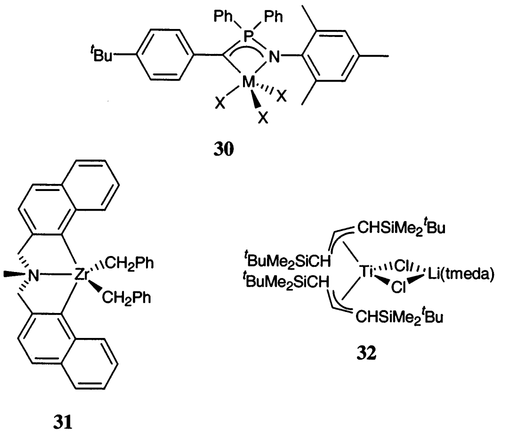


Figure 6. Non-Cp carbon-based ligands.

for the copolymerization of ethylene with 1-hexene (792 g mmol^{-1} h^{-1} bar) as well as for the polymerization of propylene (4766 g mmol^{-1} h^{-1} bar). In both homopolymerization reactions, high-molecular-weight polymer is formed with M_w(PE) > M_w(PP).

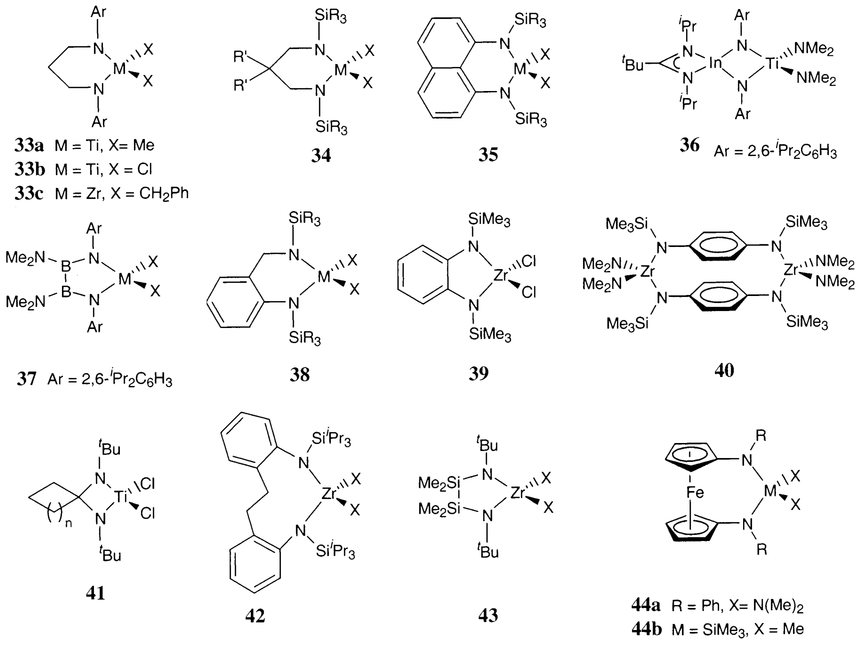
4. Non-Cp Carbon-Based Ligands

Group 4 metal complexes containing formally carbon-based anionic donors are collected in Figure 6. Zr and Ti complexes of the types **30**[93] and **31**[94] (in combination with [CPh$_3$][B(C$_6$F$_5$)$_4$]) give low activities for the polymerization of ethylene and propylene, respectively. Elastomeric PP is obtained using the bis-allyl complex **32** with moderate activities. A dynamic equilibrium between η^1- and η^3-coordination of the allyl ligand, forming C_2- and C_{2v}-symmetrical active sites, is believed to direct the PP microstructure (see also **71**, Figure 12).[95]

B. Chelating Amides and Related Ligands

1. Diamide Ligands

In 1996, McConville and co-workers reported highly active catalysts for the polymerization of higher α-olefins, with chelating diamide complexes of titanium bearing bulky 2,6-disubstituted phenyl substituents (**33**, Figure 7).[96,97] When activated with B(C$_6$F$_5$)$_3$, the Ti dimethyl complex **33a** is able to polymerize 1-hexene at room temperature in a living fashion, although the activity is dramatically reduced compared to that achieved upon activation with MAO. Subsequently, it was established that the polymerization of 1-hexene proceeds via a 1,2-insertion mechanism.[98] Uozumi and co-workers have employed the Ti dichloride complex **33b**, in combination with different cocatalysts such as Al^{i}Bu$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$], to copolymerize ethylene with 2-butene[99] and to polymerize propylene,[100,101] both with low to moderate activities. In the latter case, the polymerization proceeds via a 1,2-insertion mechanism, and at high propylene concentrations, or in the presence of cyclohexene, isotactic PP is obtained ([mmmm] up to 83%). The stereospecificity is believed to be due to enantiomorphic site control as a result of the coordination of cyclohexene or a second propylene molecule to the active species, as illustrated by the second-order dependence of the rate of formation of isotactic polymer on propylene pressure.[101] The "living" polymerization of propylene using **33b**, with moderate yields, was reported when dried MMAO as cocatalyst was employed.[102] The molecular weight of the polymer increases linearly with time and conversion, and molecular weight distributions are quite narrow (PDI 1.1−1.4). The Zr dibenzyl derivative **33c**, containing perfluorinated aryl substituents, shows only low ethylene polymerization activity with MAO cocatalyst;[103] slightly higher activities were obtained with the *N*-silyl Zr and Ti derivatives **34**.[104,105] The low activity of **34** might be due to catalyst deactivation through ligand degradation by MAO or TMA[104] and is possibly related to the instability of other silylamido-zirconium dialkyl complexes (see Scheme 1).[106] On the other hand, high activities of up to several hundred g mmol^{-1} h^{-1} bar^{-1} can be obtained with the more rigid silyl-substituted diamide titanium com-



33a M = Ti, X= Me
33b M = Ti, X = Cl
33c M = Zr, X = CH$_2$Ph
34
35
36 Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
37 Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
38
39
40
41
42
43
44a R = Ph, X= N(Me)$_2$
44b M = SiMe$_3$, X = Me

Figure 7. Chelating diamide ligands.

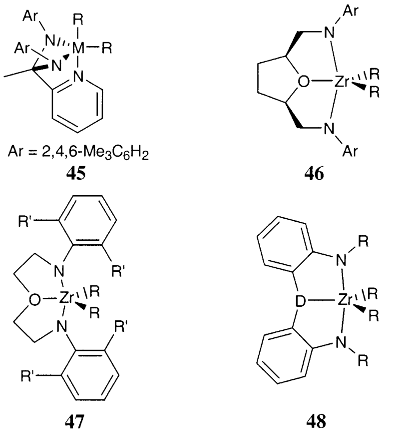
plexes **35**/MMAO in the polymerization of ethylene,[107,108] as well as for the copolymerization of ethylene with α-olefins.[109,110] Patton and co-workers have reported the diamide complexes **36**[111] and **37**.[112] Both of these catalysts give high-molecular-weight polyethylene-*co*-1-octene with high activities, though broad molecular weight distributions are obtained, believed to be due to the formation of multiple active sites.

Low activities for ethylene homopolymerization were reported for chelating diamide complexes of type **38**,[113,114] **39**,[115] **40**,[116] and **41**.[117] Higher activities are observed for zirconium complexes of type **42**, though they are measured only over very short run times.[118] A strong activator effect is observed for precatalyst **43**. Its dichloride derivative shows low activity for the polymerization of ethylene when activated with MAO,[119] whereas the analogous dibenzyl complex, in combination with [CPh$_3$][B(C$_6$F$_5$)$_4$], oligomerizes ethylene to α-olefins with activities up to 500 g mmol^{-1} h^{-1} bar^{-1}.[120] This highlights a general trend for chelating diamide complexes, which is a pronounced dependence of activity *and* selectivity on the nature of the cocatalyst and solvent. Assuming cationic alkyl complexes as the active species for complexes **33**–**44**,[121] highly Lewis acidic three-coordinate metal centers are formed after activation. In some cases they were found to be easily deactivated by interaction with the solvent; hence, lower activities are observed for **33**–**35** when the polymerization reaction is carried out in toluene rather than in alkanes or neat alkenes.[98,104,109] Bulkier cocatalysts (MMAO vs MAO or [CPh$_3$][(B(C$_6$F$_5$)$_4$] vs B(C$_6$F$_5$)$_3$) also lead to higher activities for catalysts **33** and **35**, probably due to reduced cation–anion interactions in the active species.[102,109] Collectively, these observations suggest that precatalysts bearing amido ligands are more sensitive than most to the polymerization conditions, especially the solvent and the nature of the activator or scavenger.

The ferrocenyl-bridged complexes of the type **44** offer the possibility of redox-tunable olefin polymerization catalysts. The Zr and Ti complexes **44a** are active for the polymerization of ethylene, though polymer data have yet to be reported.[122] In the case of the Ti dimethyl complex **44b**, cationic derivatives arising from its reaction with B(C$_6$F$_5$)$_3$ or [CPh$_3$][B(C$_6$F$_5$)$_4$] have been isolated and shown to oligomerize ethylene with an activity of up to 100 g mmol^{-1} h^{-1}, the activity being strongly dependent on the nature of the Lewis acid.[123,124] Results have yet to be reported on the influence of the redox center on polymerization activity and selectivity.

2. Diamide Ligands with an Additional Donor

With the aim of forming more stable, four-coordinate alkyl cations, chelating diamide ligands with an additional donor, such as in complexes **45**,[125,126] **46**,[127] **47**,[128] and **48**[129–135] (Figure 8), have been investigated by Schrock and co-workers. All are active catalysts for the polymerization of 1-hexene in combination with a suitable borane activator. Whereas **47** exhibits a significant amount of β-hydrogen transfer as a chain-termination mechanism,[136] the dimethyl complex **48** (with D = O, R = ^{t}Bu), activated by [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], produces poly(1-hexene) at 0 °C with narrow polydispersities, indicative of a living system.[132–135] The same ligand has also been attached to yttrium, but the resulting complex is unreactive toward olefins.[137] Changing the central donor in **48** from oxygen to sulfur reduces the thermal stability of the dimethyl complexes.[138] The living polymerization of 1-hexene can also be achieved with the hafnium derivative of **45** (with R = ^{i}Bu) when activated with [CPh$_3$][B(C$_6$F$_5$)$_4$] at 10 °C.[125,126]



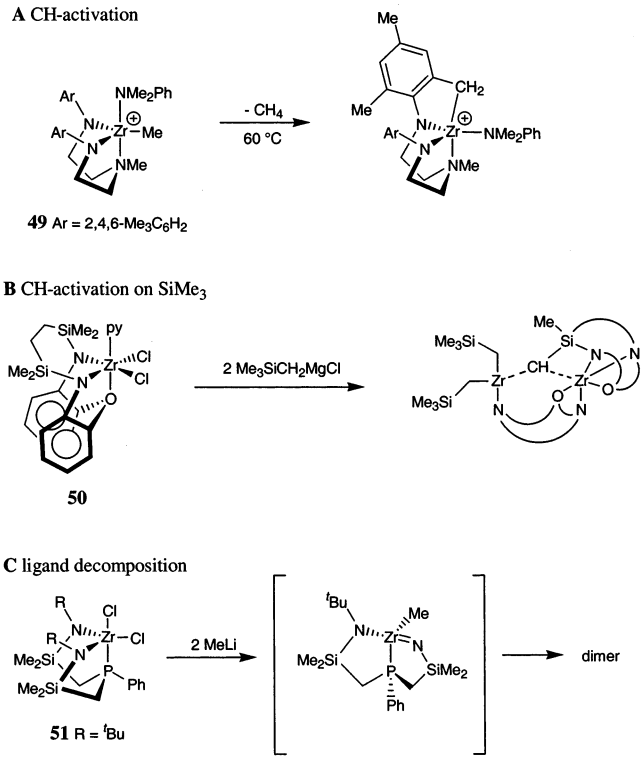
45 **46** **47** **48**

Figure 8. Chelating diamide ligands with an additional donor.

The polymerization activities of the chelating diamide zirconium and titanium complexes are generally found to be closely related to the stability of the corresponding dialkyl complex and the active species derived therefrom, believed in all cases to be an alkyl cation. In the family of chelating diamide catalysts, three main deactivation processes have been identified (Scheme 1).

The cationic Zr alkyl **49**,[139] bearing mesityl substituents on the amido nitrogen donors, decomposes at elevated temperatures via CH activation of the ortho methyl group, releasing methane in the process (Scheme 1A).[140] This catalyst decomposition competes in a polymerization reaction with the formation of poly(1-hexene); hence, the polymerization with **49** does not proceed in a living manner.[141] Using chloride substituents in the 2,6-position of the amido-phenyl ring can circumvent the problem of CH activation. They are sterically equivalent to the methyl groups, but no C–H activation can occur, and now a living system for the polymerization of 1-hexene is obtained.[142] Many of the chelating diamide complexes discussed here, as well as those reviewed previously,[12] contain silyl groups attached to the amido nitrogen-donor atom, either in a terminal position or within the ligand backbone. The silicon-methyl group can also be subjected to C–H activation, leading again to catalyst deactivation (Scheme 1B).[130] A similar reaction was observed by Horton and co-workers for the cationic diamido-donor zirconium complex [{(Me$_3$SiNCH$_2$CH$_2$)$_2$NSiMe$_3$}-ZrCH$_2$Ph][PhCH$_2$B(C$_6$F$_5$)$_3$],[143] and by Lappert and co-workers for **39** upon reaction with 2 equiv of MeLi.[115] The

Scheme 1. Catalyst Decomposition in Chelating Diamide Complexes



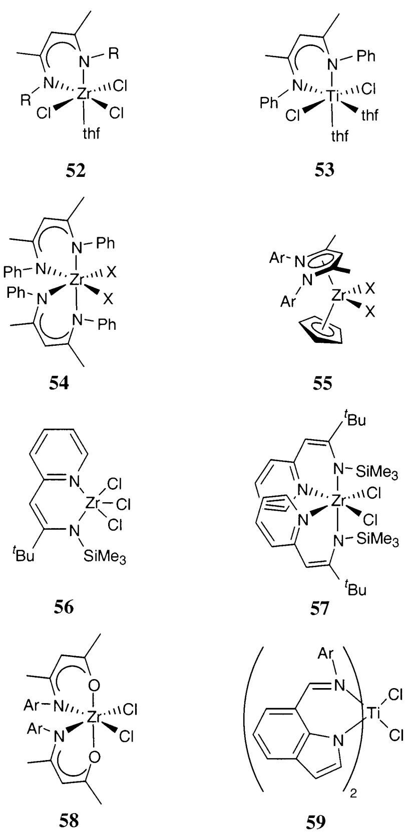


Figure 9. β-Diketiminates and related six-membered chelate ligands.

presence of silicon is also believed to be responsible for the instability of **51** upon alkylation (Scheme 1C).[106] A similar "silicon-induced" ligand degradation is assumed to cause the low activity of **34** in the polymerization of ethylene[104] and might also be responsible for the low to moderate activities of other diamido Group 4 catalysts with silicon-alkyl substituents described here and elsewhere.[12] The generally facile synthesis of Si-based amido ligands makes them readily accessible targets, but, with the recent development of Pd-catalyzed N-arylation chemistry, new bulky amido ligand systems without silicon are now more readily accessible.[144−147] The coordination chemistry of Group 4 metal amides has also been the subject of a recent review.[148]

3. β-Diketiminates and Related Six-Membered Chelate Ligands

β-Diketiminate or "nacnac" ligands, with bulky N-substituents, have recently been successfully used to stabilize a variety of transition and main group metal complexes with low coordination numbers.[149] At the same time, a number of examples of active ethylene polymerization catalysts with early transition metals bearing β-diketiminate groups, and related six-membered chelate ligands, have been reported, but olefin polymerization activities are generally moderate to low. Complex **52** (with R = Me, Figure 9)[150] shows an activity of 45 g mmol^{-1} h^{-1} bar^{-1}; a similar activity was obtained with the related mono(β-diketiminate) Ti^{III} complex **53**.[151] By using bulkier mesityl N-substituents, Budzelaar et al. were able to isolate the base free, tetrahedral Ti^{III} dimethyl analogue to **53**, but its reactivity toward α-olefins is low.[152] A slight improvement in activity is observed for the bis(β-diketiminate) Zr complex **54** (Ar = Ph).[153] Interestingly, the β-diketiminate ligand is also found in the η^5-coordination mode, as shown in **55**.[154] This transforms the ligand into a 6e$^-$ donor, to give a metallocene-related complex which exhibits activities up to 2200 g mmol^{-1} h^{-1} bar^{-1} when electron-withdrawing p-$CF_3C_6H_4$ groups are attached to the β-diketiminate nitrogen atoms.[153] Complex **56**, in which one side of the β-diketiminate is replaced by a pyridine ring, has an activity for the polymerization of ethylene of 75 g mmol^{-1} h^{-1} bar^{-1}, which is an order of magnitude higher than that of the bis-ligand complex **57**. Only moderate activity is observed for the related β-ketoiminate complexes of the type **58** for the oligomerization and polymerization of ethylene.[155,156]

Active catalysts for the living polymerization of ethylene at room temperature are obtained with titanium complexes of the type **59**, based on 7-arylimino-indole ligands, which also form six-membered chelates.[157] The highest activity (1140 g mmol^{-1} h^{-1} bar^{-1}) is observed with the electron-withdrawing pentafluorophenyl group attached to the imino nitrogen atoms.[158]

4. Iminopyrrolides and Related Five-Membered Chelate Ligands

The synthesis and olefin polymerization activity of Group 4 metal complexes with imino-pyrrolide ligands

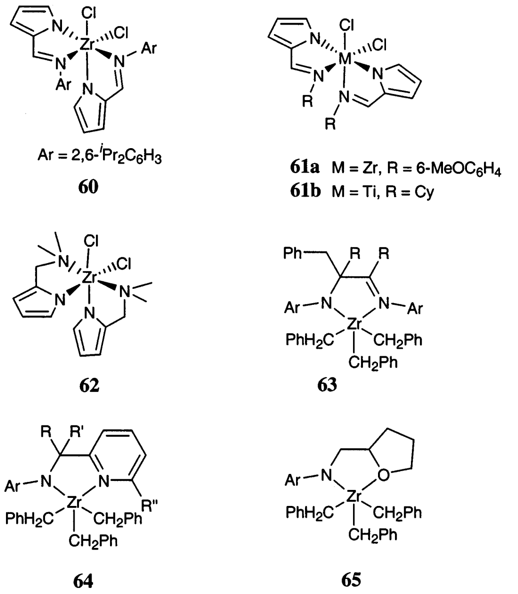


Figure 10. Imino-pyrolide and related five-membered chelate ligands.

(**60** and **61**, Figure 10) have been reported by Fujita[159-161] and Bochmann[162] and their co-workers. X-ray analyses of these complexes, as well as the related amino-pyrrolide complex **62**,[163] show in all cases a cis configuration of the chloride ligands. The arrangement of the ancillary imino-pyrrolide ligands around the metal center depends on the nature of the metal and the steric bulk of the substituents on the imino nitrogen donors. For the Zr-based complexes, both cis (**60**, **62**) and trans (**61a**) configurations of the pyrrolide donors are observed, whereas the pyrrolide moieties in Ti complexes of the type **61** are exclusively trans. In ethylene polymerization studies, it was found that the Zr complexes **60**–**62** are only moderately active for the polymerization of ethylene, whereas an activity of up to 14 000 g mmol^{-1} h^{-1} bar^{-1} can be obtained for the Ti complex **61b**.[161] Complex **61b** is also highly active for the living copolymerization of ethylene and norbornene, producing high-molecular-weight polymer with a molecular weight distribution of 1.16 and approximately 50:50 comonomer content.[164]

Related five-membered Zr amido systems for the polymerization of ethylene (**63**) have been disclosed in the patent literature.[165] Nucleophilic attack of Zr(benzyl)$_4$ on the neutral imino moiety of an added α-diimine ligand forms the precatalysts, which are then activated with MMAO. Activities of up to 6100 g mmol^{-1} h^{-1} bar^{-1} are reported for **63** for the polymerization of ethylene. Higher activities can be achieved for the copolymerization of ethylene with 1-hexene using **64** and **65**.[166,167] The activity is strongly dependent on the size of the aryl substituent. The highest activity is observed for Ar = 2,6-^{i}Pr-C$_6$H$_3$, whereas more bulky or less bulky substituents (Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$ or Ph) result in greatly reduced activities. Related Hf complexes of the types **64**[168] and **65**,[169] with a variety of cocatalysts, were also employed in the copolymerization of ethylene with styrene and 1-octene.

5. Amidinates and Related Four-Membered Chelate Ligands

Group 4 metal complexes based on amidinate ligands such as **66** and **67** (Figure 11) have had a long-standing presence in olefin polymerization catalysis.[170] More recently, Eisen and co-workers reported the formation of isotactic PP using tris(amidinate) Zr complexes bearing chiral N-substituents,[171] or with bis(amidinate) complexes **66** bearing achiral substituents R at higher propylene pressures.[172] At lower propylene pressure, epimerization becomes faster than the stereoregular insertion of propylene, and atactic polymer is thus formed.[173,174] Unsymmetrically substituted amidinate complexes of the type **67** (R ≠ R′), reported by Jayaratne and Sita,[175] are moderately active for the polymerization of 1-hexene after activation with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], but at low temperature the polymerization proceeds in a living manner with good stereocontrol to form isotactic (>95%) poly(1-hexene). The polymerization of vinylcyclohexane with high activity has also been described.[176] The related bis(iminophosphonamide) complex **68** has been reported by Collins and co-workers and shows an ethylene polymerization activity of 1400 g mmol^{-1} h^{-1} bar^{-1}, substantially higher than obtained for bis-amidinate complexes of the type **66**.[177] Binuclear oxalic amidinate complexes of Ti and Zr (**70**) have been reported by Green and co-workers and show moderate activities for the polymerization of ethylene; the activity can be increased by prealkylation of the dimethylamide complexes with TMA or Al^{i}Bu$_3$.[178]

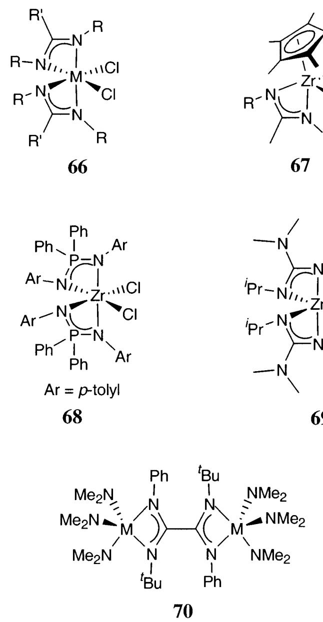
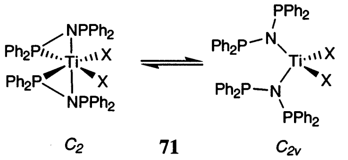


Figure 11. Amidinates and related four-membered chelate ligands.

Sterically related to the amidinate ligand is the guanidine ligand, as shown in complex **69**, but this ligand offers the possibility for an enhanced resonance stabilization of a cationic metal center. Precatalyst **69** exhibits a higher ethylene polymerization activity (340 g mmol^{-1} h^{-1} bar^{-1}) compared to its amidinate relatives.[179] Activities of up to 800 g mmol^{-1} h^{-1} bar^{-1} have been disclosed in the patent literature for Ti and Zr complexes bearing heterocyclic guanidinate-type ligands.[180]

6. Amide Ligands Forming Three-Membered Chelates

With a view to forming catalysts for the polymerization of propylene to elastomeric PP, the phosphinimide complex **71** (X = Cl) was prepared by Eisen and co-workers (Figure 12).[181] In the presence of MAO, a rapid and dynamic equilibrium between the octahedral C_2-symmetric and the tetrahedral C_{2v}-symmetric structure occurs, inducing the formation of isotactic and atactic polymer, respectively. The rapid and dynamic interconversion of these two structures leads to elastomeric PP.[173]



C_2 **71** C_{2v}

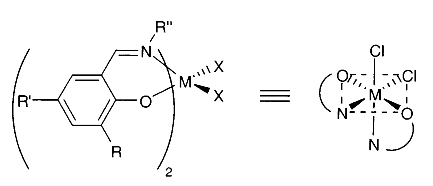
Figure 12. Amide ligands forming three-membered chelates.

C. Chelating Alkoxides, Aryloxides, and Related Ligands

1. Salicylaldiminato Ligands

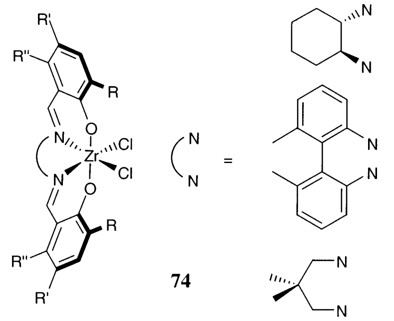
A Zr ethylene polymerization catalyst bearing two salicylaldiminato-type ligands was first reported by Floriani and co-workers in 1995, but the ethylene polymerization activity was very low.[182] Fujita and co-workers at Mitsui Chemicals developed these ligands further and reported in a series of publications new highly active Group 4 olefin polymerization catalysts of the general types **72**[183−199] and **73** (Figure 13).[200] In the polymerization of ethylene, the activity of the catalyst and the molecular weight of the polymer are highly dependent on the nature of the metal and the sizes of the group (R″) attached to the imino nitrogen atoms and the ortho substituent R in **72**. In a comparative study, it was found that for complex **72a** (R = ^{t}Bu, R′ = H, R″ = Ph), the activity decreases in the order M = Zr ≫ Hf > Ti.[186,187] Increasing the size of the imino substituents has a pronounced effect on the activity of the catalyst and the molecular weight of the polymer. Comparison of ethylene polymerization activities for complexes **72b** (M = Zr, R = ^{t}Bu, R′ = H) reveals a dramatic decrease in activity following the order R″ = Ph ≫ 2-Me-C_6H_4 ≈ 2-^{i}Pr-C_6H_4 ≫ 2-^{t}Bu-C_6H_4.[185] The molecular weight of the polymer produced increases in the same order. There is also a pronounced effect of the size of the *o*-phenoxy substituent R on polymerization activity. Increasing the steric bulk in this position leads to an increase in activity. Thus, complex **72c** (M = Zr, R′ = OMe, R″ = cyclohexyl), with a very bulky *o*-cumyl substituent R, produces PE, under optimized conditions, with an activity of 800 000 g mmol^{-1} h^{-1} bar^{-1}.[191] The higher activity is believed to arise from improved cation−anion separation in the active species as well as increased protection of the oxygen donor toward electrophilic attack by TMA (present in MAO).[185,186] Increasing the size of the imino substituent R″ has a two-fold effect: steric congestion close to the active site reduces the polymerization rate as well as the rate of β-hydrogen transfer; thus, higher molecular weight polymer is obtained, but at lower rates.[186]

Precatalysts of type **73** in combination with MAO are only moderately active for the polymerization of ethylene and some 2 orders of magnitude lower than for the related Ti complex of the type **72**.[200] In this case, variation of the steric bulk of the *o*-phenoxy substituent has very little effect on the polymerization activity. DFT calculations on the active species suggest that the ligands in **73** do not adopt the C_2-symmetric coordination mode observed for all structurally characterized highly active precatalysts of the type **72**, where a trans configuration of the phenoxy donors and cis configuration of the chloride ligands, which lie trans to the imino donors, are found (see Figure 13).[183−185] In the proposed active species derived from **73**, the cis-located polymer chain and



C_2, *cis* (Cl-Cl), *trans* (O-O)

72a R = ^{t}Bu, R' = H, R'' = Ph
72b M = Zr, R = ^{t}Bu, R' = H
72c M = Zr, R' = OMe, R'' = Cy



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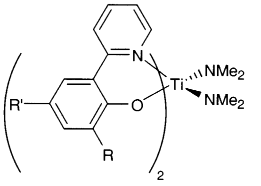

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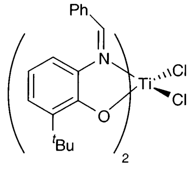

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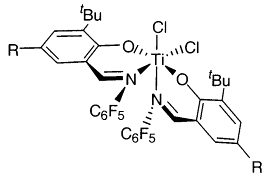

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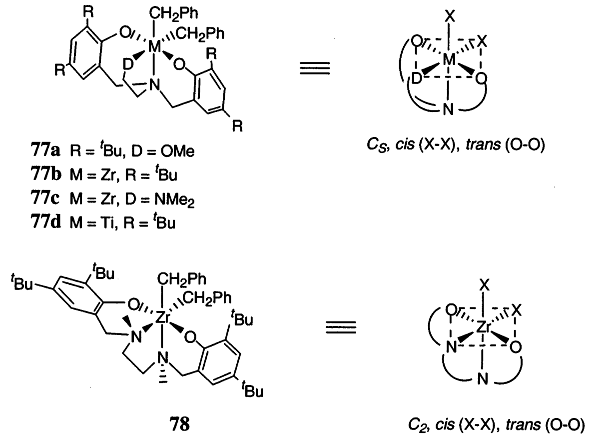
Figure 13. Salicylaldiminato and related ligands.

ethylene coordination site are trans to the phenoxy donors. In such a configuration, the ortho substituent to the phenoxy donor R is pointing away from the active sites, explaining why it then exerts little influence on polymerization activity.[200] Erker and co-workers also prepared Ti and Zr complexes of the type **72** with no substituent in the position ortho to the phenoxy donor.[201] Only moderate polymerization activities are obtained with MAO as cocatalyst, indicating again the necessity for steric bulk in this position to achieve high activities. The related complexes **74** are also only moderately active for the polymerization of ethylene.[202,203] Similar moderate activities are obtained with mixed-ligand salicylaldiminato-Cp Ti complexes.[204] Fujita and co-workers have shown that the exocyclic imine Ti derivative **75** gives a highly active ethylene polymerization catalyst on activation with MAO or ^{i}Bu$_3$Al/[CPh$_3$][B(C$_6$F$_5$)$_4$], affording high-molecular-weight PE.[205]

The success of bis(salicylaldiminato) Group 4 metal complexes is not limited to the polymerization of ethylene. The Ti precatalyst of the type **72a**, when activated with ^{i}Bu$_3$Al/[CPh$_3$][B(C$_6$F$_5$)$_4$], polymerizes 1-hexene to atactic, high-molecular-weight poly(1-hexene) with high activity.[189] Furthermore, the living polymerization of ethylene[192,193] and propylene[195,196,206,207] at room temperature has been achieved with precatalysts of the type **76**. The activity for ethylene polymerization is high, whereas in the case of propylene only moderate activities are found, but the polymerization proceeds in a highly syndiospecific manner.[195,196,207] The detailed mechanism for the polymerization and the nature of stereocontrol have yet to be fully elucidated, but polymer end-group analysis reveals a predominantly 2,1-insertion mechanism during chain growth, leading to the formation of syndiotactic PP by a chain-end-controlled mechanism.[194,206−209] The utility of the living polymerization system has been demonstrated in the synthesis of a diblock copolymer of the type *syndio*-poly(propylene)-*block*-poly(ethylene-*co*-propylene).[190,207]

2. Bis(phenoxy) Amine Ligands

Other new and highly successful catalysts for the polymerization of 1-hexene are the bis(phenoxy)-amino catalysts derived from **77** and B(C$_6$F$_5$)$_3$, introduced by Kol and co-workers.[210,211] Activities of up to 50 000 g mmol^{-1} h^{-1} are reported for the Zr derivative **77a** (R = ^{t}Bu, D = OMe, X = CH$_2$Ph, Figure 14).[212] Similar to the salicylaldiminato complexes described in the previous section, all structurally characterized precatalysts **77** adopt a *cis*-(X−X), *trans*-(O−O) ligand configuration.[213,214] The activity decreases for D = NMe$_2$ or OMe in the order Zr > Hf ≫ Ti.[212,215] The nature of the additional donor D has a pronounced effect on the polymerization activity and the molecular weight of the resultant polymer. In the absence of an additional donor, only moderate activity is obtained.[211] In the Zr series **77b**, the activity decreases in the order D = OMe > NMe$_2$ > SMe > py > NEt$_2$.[212,213] Surprisingly, reducing the size of the phenoxy ortho substituent (R = Me vs ^{t}Bu) in **77c** has very little effect on the activity for the polymerization of 1-hexene.[213] The polydispersity of the polymer is generally low, but the Zr complexes **77** do not polymerize 1-hexene in a living manner. By contrast, the Ti analogues **77d** (with D = NMe$_2$[215] or D = OMe[216]) produce very narrow dispersity poly(1-hexene), albeit at lower rates. The living nature of the polymerization reaction is demonstrated by the synthesis of the block copolymer poly(1-hexene-*block*-1-octene) by sequential addition of the monomers. The related bis(phenoxy)-bis(amino) Ti complex **78**, activated with B(C$_6$F$_5$)$_3$, also polymerizes 1-hexene in a living fashion with similarly moderate activity.[217] The resultant polymer is >95% isotactic. No mechanistic conclusions have been reported to date, but the C_2-symmetric ligand environment in the precatalyst, combined with the *cis*-(X−X) arrangement of the benzyl groups, suggests that enantiomorphic site control may account for the stereoselectivity. Similar activity and degree of stereocontrol can be achieved in the polymerization of propylene, but in this case fast monomer-assisted β-hydrogen elimination as a chain-termination mechanism is observed.[218]



77a R = ^{t}Bu, D = OMe
77b M = Zr, R = ^{t}Bu
77c M = Zr, D = NMe$_2$
77d M = Ti, R = ^{t}Bu

78

Figure 14. Bis(phenoxy)amine ligands.

3. Other Aryloxide, Alkoxide, and Thiolate Ligands

A variety of complexes based on ligands bearing aryloxide, alkoxide, and thiolate donors are summarized in Figure 15. Complexes of the type **79** show activities up to 230 g mmol^{-1} h^{-1} bar^{-1} for the polymerization of ethylene.[219] Complexes **80**,[220] **81**,[220] **82**,[221] and **83**[222] as well as Ti complexes supported by calix[4]arene ligands[223] are only moderately active for the polymerization of ethylene. The ferrocenyl-based dithiolate Zr and Ti and complexes of the type **84** give similarly moderate to low ethylene polymerization activities.[224] Only a single ethylene insertion is observed for **85** after activation with [CPh$_3$][B(C$_6$F$_5$)$_4$], and a stable cationic (η^1:η^6-CH$_2$CH$_2$CH$_2$-Ph)Zr complex is obtained.[225] A similar observation was made for the {Me$_2$Si(NCMe$_3$)$_2$}Zr(CH$_2$Ph)$_2$ complex studied by Horton and deWith.[226] Conversely, the Ti complex **86**, containing a related bis(alkoxide)-pyridine ligand, produces high-density PE with high activity.[227] Simple Zr and Ti bis(acetylacetonate) dichloride complexes produce elastomeric PP with moderate activities.[228]

4. Aryloxide and Alkoxide Ligands in Combination with Cp

The mixed-ligand complexes **87**,[229] **88**,[230] and **89**[204] (Figure 16) exhibit moderate activities for the polymerization of ethylene. Whereas for **88** the Zr com-

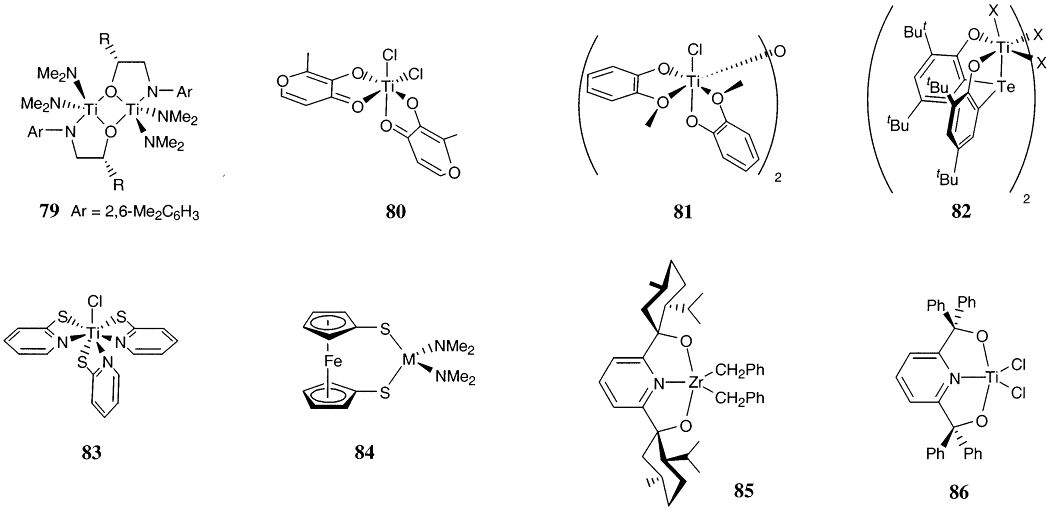


Figure 15. Other aryloxide, alkoxide, and thiolate ligands.

plexes generally give higher activities than their Ti analogues, little metal dependence is observed for **87**. Ti complexes of the type **90** have been reported by Nomura and co-workers,[231] and a series of related Zr complexes have been described by Otero and co-workers.[232] They generally show very high ethylene polymerization activities, the Zr complex **90** (with R = ^{t}Bu, R′ = Me$_5$) being the most active (4260 g mmol^{-1} h^{-1} bar^{-1}). High activities are also obtained for the Ti complexes in the copolymerization of ethylene with α-olefins and styrene, as well as for the homopolymerization of 1-hexene.[233−240] The highest activities are generally observed for bulky aryl substituents, where R = ^{i}Pr or ^{t}Bu. The coordination chemistry of Cp ligands with pendant alkoxide and aryloxide donors has been the subject of a recent review.[241]

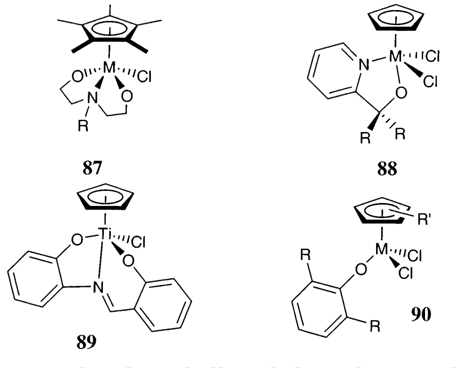


Figure 16. Aryloxide and alkoxide ligands in combination with Cp.

V. Group 5 Catalysts

Active Group 5 metal catalysts for the polymerization of olefins reported prior to 1998 were generally based on high-valent metal precursors.[12] In most cases, the isolobal relationship between the monoanionic Cp ligand and dianionic fragments[242] such as imido ligands was exploited to generate metallocene-related analogues of Group 4 metal catalysts, with high-valent cationic 14-electron alkyls as the proposed active species. More recently, a number of Group 5 metal catalysts for the polymerization of olefins with the metal in its lower oxidation states, +IV and +III, have been reported. The oxidation state of the active species is an important factor for the polymerization activity of Group 5 metal complexes, and in many cases catalyst deactivation is accompanied by a change in metal valency. Even though the active species after addition of the cocatalyst might contain a metal center in an oxidation state different from that of the precatalyst, it seemed most appropriate to review Group 5 metal catalysts according to their starting oxidation state.

A. Precatalysts in the +V Oxidation State

Cp-imido vanadium complexes give only low to moderate ethylene polymerization activities, mainly due to short catalyst lifetimes as a result of bimolecular decomposition processes.[12,243] Supporting the imido catalysts on a polystyrene resin (**91**, Figure 17) results in longer catalyst lifetimes and high-molecular-weight PE.[244] Non-Cp mono-imido vanadium complexes of the type **92** were prepared by Nomura and co-workers.[245] These may be viewed as being isolobal to the Cp-aryloxide Ti$^{\text{IV}}$ complexes of the general structure **90** (see Figure 16). The ethylene polymerization activity observed for **92** (with R = 2,6-^{i}Pr$_2$C$_6$H$_3$, R′ = H) of 120 g mmol^{-1} h^{-1} bar^{-1} is somewhat lower than that observed for the Cp*-substituted Ti complex **90**, but the molecular weight of the polymer is greatly increased.[246] By further analogy to active Group 4 metal catalysts,[242] Chen and co-workers prepared complexes **93** and **94**.[247] The metallocene-related complex **93** gave an activity of 1200 g mmol^{-1} h^{-1} bar^{-1} for ethylene/1-octene copolymerization when activated with Al imidazolide ([HNMe(C$_{18}$H$_{37}$)$_2$][(C$_6$F$_5$)$_3$AlNC$_3$H$_3$NAl(C$_6$F$_5$)$_3$]), an order of magnitude higher than that for **94** under identical conditions. The low density of the polymer (0.898 g/mL) is consistent with a significant degree of 1-octene incorporation. The isolobal relationship between imido and η^2-bound alkyne ligands[242] has also been exploited in the design of the high-valent Nb complexes **95** and **96**. Addition of B(C$_6$F$_5$)$_3$ to the

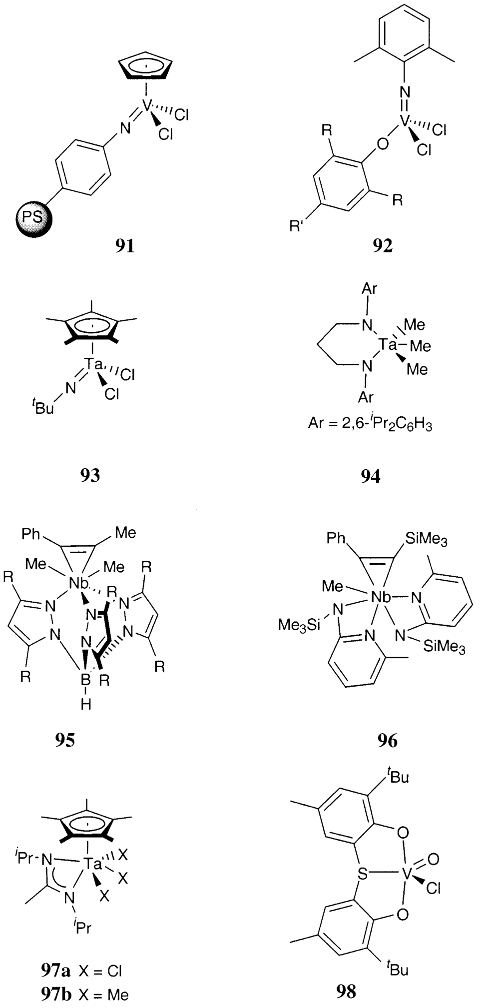


Figure 17. Pentavalent Group 5 metal precatalysts.

(amido)pyridine complex **96** results in abstraction of the methyl group and the formation of a contact-ion pair, which could be structurally characterized.[248] Addition of ethylene leads to the formation of a low-molecular-weight polymer with low activity. The ethylene polymerization activity for **95** is dependent on the size of the R substituents on the hydrido-tris(pyrazolyl)borate ligand and the nature of the co-catalyst. Activities up to 130 g mmol^{-1} h^{-1} bar^{-1} are achieved with R = Me, whereas lower activity is found for R = H, both after activation with $B(C_6F_5)_3$.[249] Treatment of the precatalyst with MAO does not result in any polymerization activity. The opposite effect is found for Ta complexes of type **97**. Activation of the dichloride complex **97a** with MAO leads to a highly active ethylene polymerization system (470 g mmol^{-1} h^{-1} bar^{-1}) and produces polymer with a narrow molecular weight distribution. On the other hand, addition of $B(C_6F_5)_3$ to the trimethyl derivative **97b** yields an inactive system.[250] $TaCl_3Me_2$ has been reported to be a precatalyst for the selective trimerization of ethylene, but with very low activity.[251]

Vanadyl phenoxide olefin polymerization catalysts have recently been reported. Takaoki and Miyatake were able to polymerize propylene using **98** with an activity of 1900 g mmol^{-1} h^{-1} in liquid monomer.[252] Substitution of the chloride ligand for O-^{t}Bu gives rise to an increase in isotacticity ([mm] = 68%).

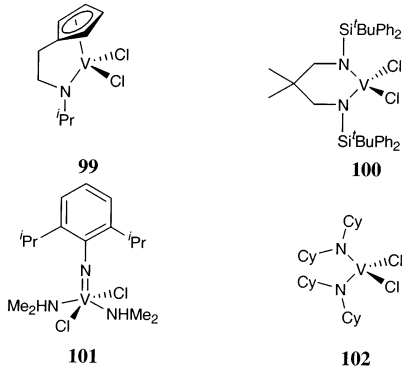


Figure 18. Tetravalent Group 5 metal precatalysts.

B. Precatalysts in the +IV Oxidation State

Among the key advances in Group 5 metal olefin polymerization catalysis has been the introduction of catalysts based on medium-valent vanadium(IV) and -(III) metal centers. The use of d^1 vanadium(IV) allows a direct comparison with isostructural d^0 complexes of the Group 4 metals. One example is **99** (Figure 18), bearing a Cp-amido or "constrained geometry" type ligand. It produces low-molecular-weight PE with an activity of 209 g mmol^{-1} h^{-1} bar^{-1}, which is less than half that observed for the isostructural Ti^{IV} complex under identical conditions.[253] A similar observation is made for the diamide complex **100**, which shows a very low activity for the polymerization of ethylene, an order of magnitude lower than that obtained with the related Group 4 metal complexes of the type **34** (Figure 7).[104] The lower activity of d^1 vanadium(IV) complexes compared to their isostructural d^0 Group 4 relatives is also seen for $[Cp_2VMe]^+$, the direct analogue of Group 4 metallocene alkyl cations; the vanadocene derivative is inactive for ethylene polymerization.[254]

Another interesting comparison can be drawn between the vanadium(IV) imido complex **101** and the more established imido complexes based on d^0 vanadium. Complex **101** is a rare example of a structurally characterized d^1 imido vanadium complex and shows an ethylene polymerization activity of 120 g mmol^{-1} h^{-1} bar^{-1} after activation with $EtAlCl_2$.[255] The somewhat lower activity with MAO is reminiscent of results obtained for d^0 Cp-imido Group 5 metal complexes.[12] The highest activity observed in the series of vanadium(IV) catalysts was reported for the simple diamide complex **102**. The polymerization of ethylene and the copolymerization of ethylene with propylene are catalyzed by **102** after activation with a variety of Al cocatalysts; an activity of 430 g mmol^{-1} h^{-1} bar^{-1} was achieved using $Et_3Al_2Cl_3$ as an activator.[256]

C. Precatalysts in the +III Oxidation State

Vanadium(III) complexes have only recently gained attention as precursors for olefin polymerization catalysis. This is perhaps surprising since simple V^{III} complexes such as $V(acac)_3$ are widely employed commercially in the synthesis of ethylene–propylene–diene (EPDM) elastomers.[257] Gambarotta and coworkers found that, for ethylene–propylene copolymerizations using a variety of substituted $V(acac)_3$

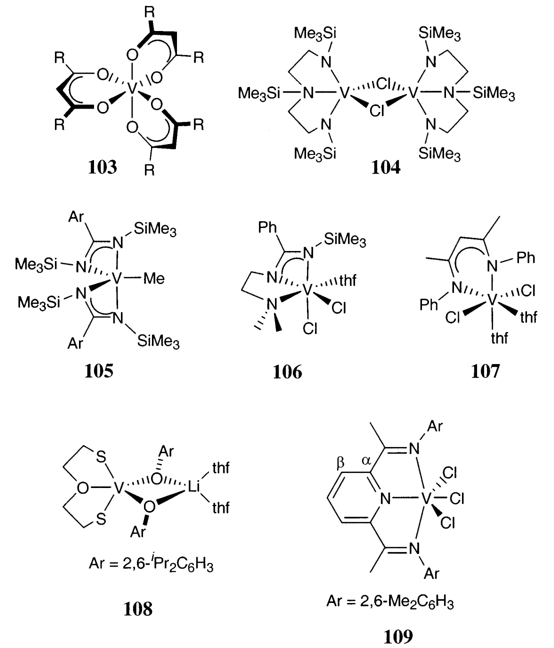


Figure 19. Trivalent Group 5 metal precatalysts.

complexes of the type **103** (Figure 19) and Et_2AlCl or $Et_3Al_2Cl_3$ as cocatalyst, activities up to 1170 g mmol^{-1} h^{-1} bar^{-1} can be achieved.[258] In the absence of monomer, the active species is unstable, and some decomposition products containing V^{II} centers could be isolated and structurally characterized. Reduction of the active species from V^{III} to V^{II} is also responsible for the short catalyst lifetime, and hence only moderate ethylene polymerization activities are found for the binuclear complex **104**.[259] Similar deactivation processes have been proposed for complexes of the type **105**, which exhibit very low activities for the formation of low-molecular-weight PE and α-olefins.[260,261] The activities and the molecular weight of the polymer are increased by incorporation of a pendant amino functionality, as shown in **106**. Now high-molecular-weight PE (M_w = 760 000) is obtained with an activity of 447 g mmol^{-1} h^{-1} bar^{-1}.[262]

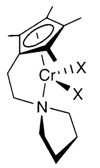
The β-diketiminate complex **107** shows only very low activity for ethylene polymerization. It is also lower than that for the isostructural Ti^{III} complex **53** (see Figure 9), following the trend observed for V^{IV} vs Ti^{IV} catalysts discussed in the previous section.[151] Complexes **108** and **109**, on the other hand, are two examples of highly active ethylene polymerization catalysts based on V^{III}. Sobota and co-workers prepared a range of dithiolate complexes, of which **108** is the most active (330 g mmol^{-1} h^{-1} bar^{-1}).[263] Similarly active catalysts are derived from **109**, as reported by Gambarotta and co-workers.[264] Here, the bis(imino)pyridine ligand is employed, which has been shown to provide highly active catalysts in combination with Fe (**133a**, Figure 23) and Co (**138**, Figure 25). In a detailed study of the system, they were able to isolate and structurally characterize alkylation products of **109** upon treatment with MAO or MeLi. Surprisingly, the first alkylation step involves a nucleophilic attack of the methyl group on the α-carbon of the pyridine ring in **109**. The resulting new V^{III} species, bearing now a bis(imino)amido ligand, is also an active catalyst when treated with MAO with an activity equal to that of **109**. Further reaction with MeLi gives rise to two products, both of which are now reduced to V^{I} and inactive for the polymerization of ethylene.[264] Bochmann and co-workers prepared bis(phosphinimide)pyridine V^{III} complexes and reported ethylene polymerization activities up to 140 g mmol^{-1} h^{-1} bar^{-1}, which is higher than the values obtained with the analogous Fe^{II} (**133m**) and Co^{II} (**139**) complexes (see sections VIII and IX).[265] Polyethylenes with very high molecular weights and broad distributions are formed.

VI. Group 6 Catalysts

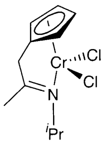
The chromium-based heterogeneous Phillips catalyst, obtained by impregnation of Cr oxides on silica, and the Union Carbide Unipol catalyst system, derived from Cp_2Cr adsorbed on silica, are both used in the large-scale industrial production of polyolefins.[266] The active species are believed to contain low-valent Cr centers. The relatively ill-defined nature of these catalysts with respect to coordination environment and oxidation state, however, has prompted considerable efforts to synthesize well-defined homogeneous Cr-based catalysts. In this context, mainly Cp-based Cr^{III} complexes stabilized with an additional neutral donor were reported prior to 1998, along with a few high-valent Cr^{VI} imido examples.[12] Computational studies have been used to explore the nature of the oxidation state in catalysts derived from Cr^{VI} bis(imido) complexes.[267,268] In more recent years, a significant amount of attention has been given to the development of homogeneous non-Cp systems. There have also been two reports of molecular catalysts for ethylene polymerization based on molybdenum, but both the bis(imido)Mo^{VI}Cl$_2$ precatalyst[269] and the Cp*(butadiene)-Mo^{III}Cl$_2$ system[270] show only very low activities.

A. Cp-Based Ligands

Some of the most significant advances in Cp-based chromium catalyst systems have been made using precatalysts that bear an additional neutral donor, either bridged or unbridged to the Cp unit. Calculations on Cr complexes of this type have shown that the presence of the donor in the inner coordination sphere of the metal is essential for activity; thus, bridged complexes generally exhibit higher activities than their unbridged counterparts.[271,272] Jolly and co-workers reported an activity of 14 800 g mmol^{-1} h^{-1} bar^{-1} for complex **110a** (Figure 20), bearing the *N*-pyrrolidine pendant donor, although reaction times are very short.[273] Lower activities were previously communicated with methyl substituents on the amino donor.[274] The dimethyl complex **110b** is also highly active for the copolymerization of ethylene with 1-hexene in neat comonomer, though much lower activities are observed in homopolymerizations of 1-hexene and propylene. Avtomonov and co-workers described a related phosphino-bridged Cp-amine system for the polymerization of ethylene with high activity.[275] Jolly and co-workers also prepared the Cp-imine Cr complex **111**, which shows an ethylene polymerization activity of ca. 1700 g mmol^{-1} h^{-1}



110a X = Cl
110b X = Me



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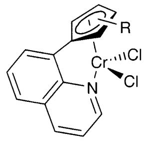

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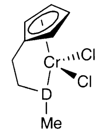

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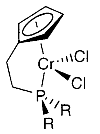

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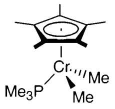

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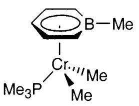

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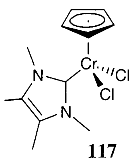

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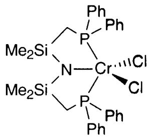
Figure 20. Cp-based Group 6 metal precatalysts.

bar^{-1}, comparable to that of the related Cp-amine complex bearing a $C_2H_4NMe_2$ sidearm. The activity can be increased when the imino functionality is incorporated into the more rigid quinoline moiety, as shown in complex **112**, which is also able to polymerize propylene to atactic polymer with moderate activity.[276,277] The bridged Cp-N-donor complexes **110**−**112** generally produce high-molecular-weight PE, with a polydispersity index between 1.5 and 4.

Other highly active ethylene polymerization catalysts bearing bridged Cp-donor ligands include the methoxy (1400 g mmol^{-1} h^{-1} bar^{-1}) and methylthio (2000 g mmol^{-1} h^{-1} bar^{-1}) derivatives of the type **113**.[273] Precatalysts with pendant phosphine donors, e.g., **114**, have also been reported by Jolly and coworkers.[278,279] They produce oligomers and low-molecular-weight PE with high activity. The presence of bulky substituents, such as cyclohexyl, on the phosphorus donor leads to increased formation of solid PE but also to lower activities. The unbridged Cp-phosphine complex **115** also produces oligomeric products after activation with MAO but at a lower rate than **114**. Whereas in the bridged complex **114**, β-hydrogen-transfer is operative as the only chain-transfer-termination step to produce oligomeric α-olefins, **115** produces linear saturated alkanes via chain transfer to aluminum.[280] Bazan and co-workers were also able to isolate and structurally characterize the cationic methyl derivative, [Cp*Cr(PMe$_3$)Me(thf)][MeB(C_6F_5)$_3$], which is believed to be the active species in this system.[281] The isoelectronic boratabenzene complex **116** is also highly active for the formation of linear PE.[282] The molecular weight is moderately high, with M_n as high as 17 000, which is substantially higher than that found for **115**; no oligomeric products are obtained. It is noteworthy that replacement of the PMe$_3$ donor by pyridine in **115** results in an inactive system, possibly due to catalyst decomposition as a result of pyridine abstraction by the MAO cocatalyst.[282] Complex **117**, in which the phosphine donor is substituted with the powerful σ-donating N-heterocyclic carbene ligand, polymerizes ethylene to solid polymer with low activity.[273] The related (N,N'-bis(mesityl)carbene)CpCr^{II}Cl complex is moderately active for the polymerization of ethylene.[283,284] Only low polymerization activity is observed with Cp-based Cr complexes bearing no additional donors.[285,286]

B. Non-Cp-Based Amide, Amine, and Phenoxy Ligands

The development of non-Cp Cr-based catalysts for the polymerization of olefins has gained increased momentum in recent years, and these catalysts are now able to match the polymerization activities seen for systems containing Cp ligands described in the previous section. Researchers at ExxonMobil have disclosed a variety of tridentate monoanionic ligands with trivalent early and late transition metals, e.g., **118**−**120** (Figure 21).[287] The highest activity (500 g mmol^{-1} h^{-1} bar^{-1}) is observed for the chromium complex **118**, containing the bis(phosphino)amide ligand introduced by Fryzuk and co-workers.[288] With this ligand, a highly active ethylene polymerization catalyst is also obtained with V^{III} centers, whereas the related Ti^{III} and Fe^{III} complexes as well as **119**[289] and **120** gave only low to moderate activities.[287] The Cr complex **118** is also active for the polymerization of propylene and for ethylene/1-hexene copolymerization.



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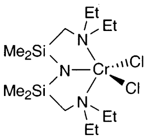

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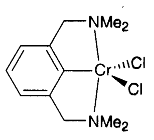

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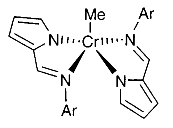

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

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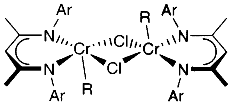

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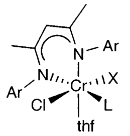


123a Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, X^L = PhCOO
123b Ar = Ph, X = Cl, L = thf

Figure 21. Group 6 metal precatalysts with anionic nitrogen- and carbon-based donors.

The imino-pyrrolide Cr complex **121**, reported by Gibson and co-workers, affords an ethylene polymerization activity of 70 g mmol^{-1} h^{-1} bar^{-1} in combination with Et$_2$AlCl.[290] Slightly lower activities

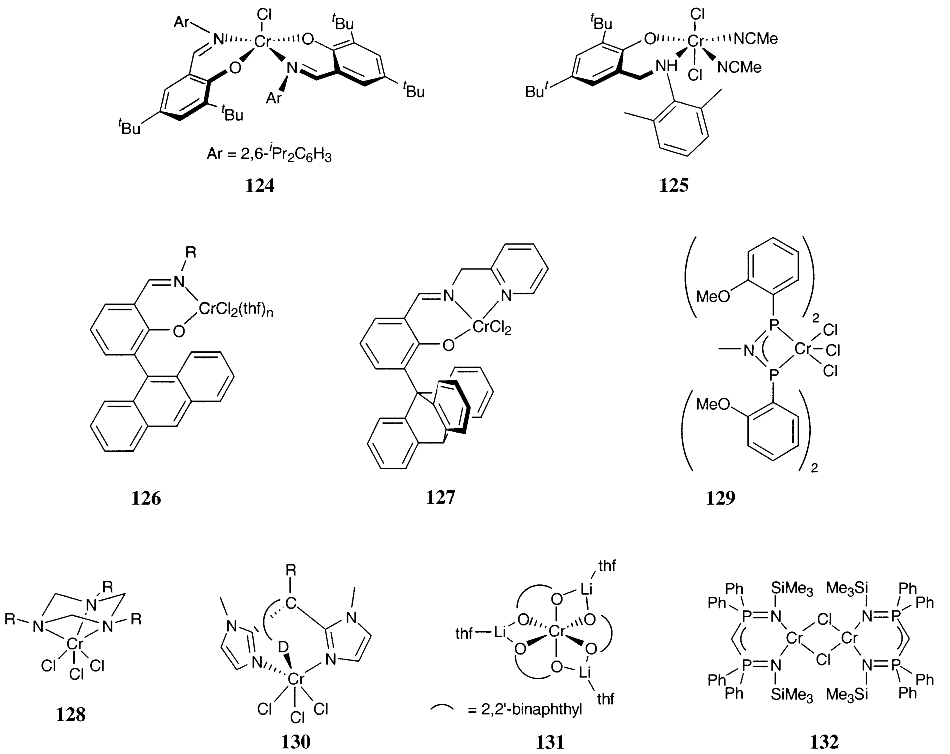


Figure 22. Group 6 metal precatalysts with aryloxide, amine, and phosphine ligands.

have been reported for the binuclear Cr complex **122** (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)[291] and for the related binuclear Cr complex bearing less bulky phenyl substituents.[292] The mononuclear β-diketiminate complexes **123a**[291] and **123b**[151] produce high-molecular-weight PE with noticeably higher activities when Et$_2$AlCl is used in place of MAO as cocatalyst. Theopold and co-workers were also able to isolate and structurally characterize a cationic alkyl derivative bearing the 2,6-^{i}Pr$_2$C$_6$H$_3$-substituted β-diketiminate ligand and reported moderate ethylene polymerization activity in the absence of cocatalyst.[293] Activation of precatalysts such as **121**−**125** with MAO generally leads to much lower activities compared to those obtained upon activation with alkylaluminum chlorides. Since an important mode of action of MAO is the abstraction of an alkyl anion from the metal precatalyst to give a cationic active site, this observation may indicate that the propagating centers are neutral, rather than cationic, alkyls. The kinetic stability of octahedral Cr^{III} centers may also play an important role if the active site possesses a pseudo-octahedral coordination geometry.

Salicylaldiminato ligands have also been employed to stabilize Cr^{III} catalysts. The square-pyramidal bischelate complex **124** (Figure 22), described by Gibson and co-workers, produces high-molecular-weight PE with an activity of 96 g mmol^{-1} h^{-1} bar^{-1}.[294] A slightly higher activity is obtained with the monochelate complex **125**, bearing a reduced Schiff-base ligand.[295] Again, Et$_2$AlCl activator affords more active catalysts than MAO. Introducing a bulky anthracenyl substituent into the ortho position allows monochelate precatalysts of the type **126** to be accessed, and these are now best activated using MAO,[296] most probably due to cationic alkyl species being formed upon activation. The most active catalyst is obtained when small substituents are attached to the imino nitrogen donor and very high-molecular-weight PE is obtained. Larger substituents, such as 2,6-diisopropylphenyl, afford low-activity catalysts. This difference has been rationalized as being a consequence of the unfavorable positioning of the isopropyl units of the large aryl groups in non-square-planar coordination geometries. High-throughput screening methodology was employed to optimize catalyst performance, and in so doing a second family of highly active catalysts was discovered, containing salicylaldiminato ligands with pendant donors and a tryptycenyl group attached to the ortho position of the phenoxy donor. The most active catalyst is derived from **127** (6970 g mmol^{-1} h^{-1} bar^{-1}), affording low-molecular-weight PE and highly linear α-olefins.

Triazacyclohexane complexes **128** have been shown by Köhn and co-workers to give highly active ethylene polymerization catalysts. Activity is dependent on the chain length of the alkyl substituent R, with a maximum of 717 g mmol^{-1} h^{-1} bar^{-1} being reported for R = *n*-dodecyl.[297] Higher activities can be achieved with a combination of AlR$_3$ and borate activators.[277] The molecular weight of the polymer (M_w) is ca. 40 000, with M_w/M_n = 2−4, but some 1-hexene, arising from ethylene trimerization, is also formed. This trimerization reaction becomes dominant for α-olefins[298] or when branched R substituents such as 3-propyl-heptyl are employed.[299] The mechanism is believed to proceed in a manner analogous to that proposed for the Phillips trimerization catalyst system.[300] Wass and co-workers at BP have described remarkably active and selective trimerization catalysts based on Cr^{III} precursors containing diphosphine ligands (**129**).[301] A bridging imido (NR) unit and aryl substituents bearing *o*-methoxy substituents play crucial roles in both the activity and the selectivity of the system. The activities seen in this system are comparable to those of the most active ethylene polymerization systems, holding out the prospect for in situ 1-hexene generation for copolymer production. Interestingly, derivatives containing diphosphines with the same aryl substituents but with $-CH_2-$ and $-CH_2CH_2-$ linking groups are inactive.

Another family of Cr complexes bearing neutral donor ligands (**130**) also form predominantly oligomeric products with ethylene after activation with MMAO, but only with low activity and little selectivity.[302] Similarly low activity has been reported for the hexakis(aryloxide) complex **131** in combination with MMAO.[303] Simple homoleptic Cr^{III} and Cr^{IV} alkyls CrR_n ($R = CH(SiMe_3)_2$, with $n = 3, 4$) and the tris(amide) complex $Cr[N(SiMe_3)_2]_3$ also polymerize ethylene with low to moderate activity, respectively.[304] Wei and Stephan reported an ethylene polymerization activity of 60 g $mmol^{-1}$ h^{-1} bar^{-1} for the dimeric Cr^{II} complex **132**, affording high-molecular-weight polymer with a broad molecular weight distribution.[305]

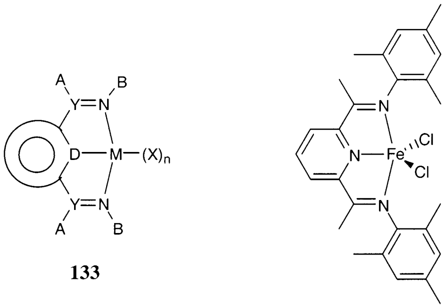
VII. Group 7 Catalysts

Despite enormous efforts in industrial and academic research laboratories to discover new olefin polymerization catalysts, no major breakthrough has yet been achieved using metals of Group 7. Some recent reports describe the ethylene and propylene polymerization activity of complexes such as $Mn(acac)_3$, Cp_2Mn, (salen)MnCl, and (salicylaldiminato)MnF, but only trace amounts of polymer were isolated.[306,307] Generally, several orders of magnitude lower activities are observed for Mn^{II} or Mn^{III} complexes bearing ligands which give highly active catalysts with other late or early transition metals. This is illustrated by the very low ethylene polymerization activity for the [(bis(imino)pyridine)]-$MnCl_2$ complex compared to the high activity obtained with the related Fe^{II} (**133a**, Figure 23), Co^{II} (**138**, Figure 25), and V^{III} (**109**, Figure 19) complexes.[264,308] After alkylation of the (bis(imino)pyridine)$MnCl_2$ complex, Gambarotta and co-workers were able to isolate and structurally characterize mono- and zerovalent Mn alkyl species.[309] Such reductive processes in the presence of alkylating agents might be responsible for the poor catalyst performance.

VIII. Group 8 Catalysts

A. Neutral Bis(imino)pyridine and Related Ligands

Recent advances in olefin polymerization catalysis using Group 8 metals are mainly based on developments around the bis(imino)pyridine system of the general structure **133**. This family of catalysts has attracted great interest, both in academia and in industry.[310,311] The initial discovery of these iron-based catalysts[9,10] was based on bis(imino)pyridine ligands with bulky aryl substituents, one of the most active examples being **133a** (Figure 23). The catalysts show exceptionally high activities for ethylene polymerization, producing strictly linear, high-molecular-weight polymer.[312] They also exhibit a remarkable selectivity for ethylene oligomerization to linear α-olefins when imino-aryl groups with only one small substituent such as 2-MeC_6H_4 are employed,[313,314] or when the ligand contains two differently substituted imino moieties.[315] The steric bulk provided by the substituents on the imino nitrogen donors plays a pivotal role in preventing the formation of bis-chelate complexes and controlling the rates of propagation and chain termination, thus influencing both activity and molecular weight of the polymer. In addition to β-hydrogen transfer, chain transfer to Al is also operative, resulting generally in the formation of polymer with broad and, in the presence of high MAO loadings, bimodal molecular weight distributions.[312]



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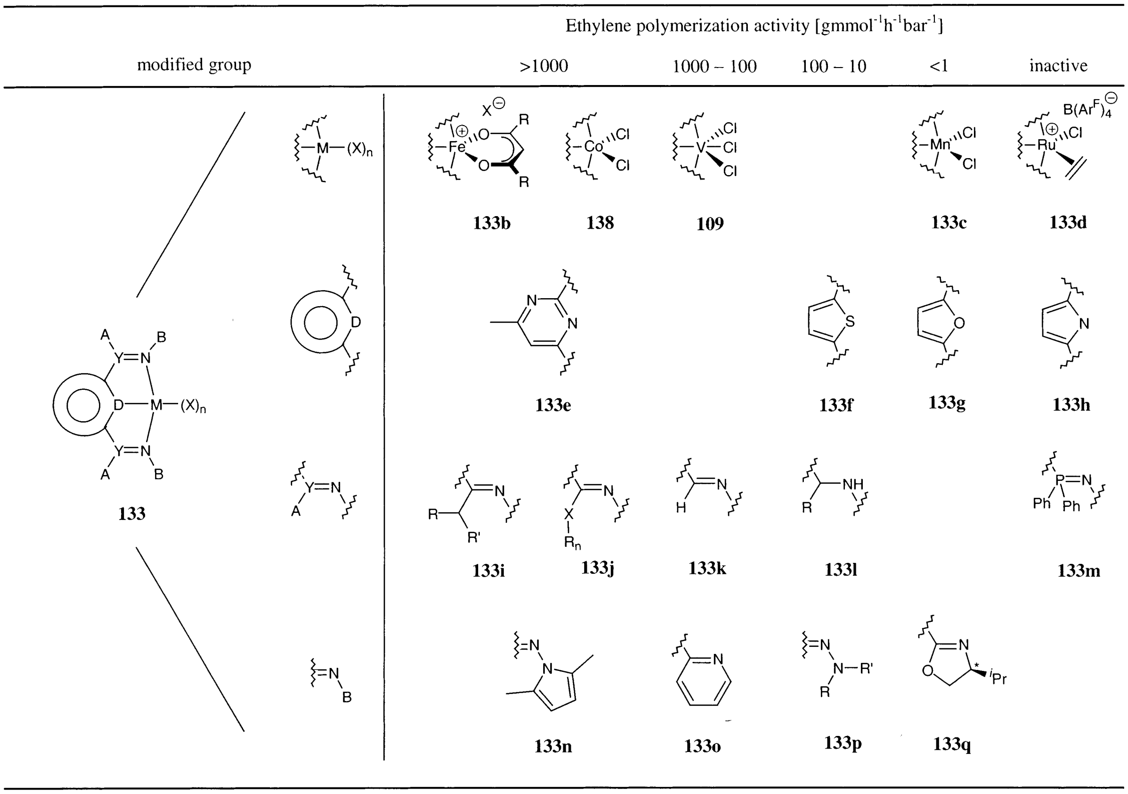
133a

Figure 23. Bis(imino)pyridine Fe complexes.

The active species for these catalysts are not as well understood as those for the α-diimine nickel and palladium systems.[316,317] By analogy to Group 4 metallocene and the Group 10 metal systems, it was initially presumed that a 14-electron cationic Fe^{II} alkyl species is formed upon activation with MAO.[312,318] A number of theoretical studies were reported based on this assumption.[319−322] Neutral Fe^{II} complexes containing TMA in the coordination sphere of the metal have also been proposed.[323] However, EPR and Mössbauer studies reveal that the starting bis(imino)pyridine Fe^{II} complex is oxidized to an Fe^{III} species upon addition of MAO.[324] It is noteworthy, in this context, that Fe^{II} and Fe^{III} precursors produce identical PE with similar activities, suggesting the presence of the same active species, whose precise nature remains undetermined.[312] Various modifications to the original bis(imino)pyridine ligand framework, metal substitution, and detailed polymerization studies have been reported.[162,264,265,325−344] The Fe-based catalysts, in conjunction with Group 4 metallocene catalysts, were also successfully employed in reactor blending experiments to produce polymer blends or linear low-density polyethylene (LLDPE) from one ethylene feed.[345−347] The reasonable lifetime of these catalysts at elevated temperatures and their suitability for adaptation to existing plant conditions have undoubtedly contributed to the large number of reports on this system in the patent literature.[348−369] A summary of the more important structural variations of **133** is provided in Table 1.

Cationic bis(imino)pyridine iron complexes of type **133b** were prepared in an attempt to isolate cationic alkyl derivatives.[327,349] These attempts were unsuc-

Table 1. Structural Variations on the Bis(imino)pyridine Fe Precatalysts 133



cessful, but the cationic complexes show high ethylene polymerization activities in combination with MAO or $AlMe_3/B(C_6F_5)_3$. In the latter case, PEs with narrower polydispersities are 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 copolymer was obtained. Other polar olefins such as vinyl acetate, acrolein, and acrylonitrile led to the deactivation of the bis(imino)pyridine Fe catalysts.[327] As discussed previously, the bis(imino)pyridine ligand also affords highly active catalysts with V^{III} centers (**109**),[264] whereas Mn^{II} complexes (**133c**) exhibit only very low activity.[308] The complexes of the higher homologue Ru^{II}, such as **133d** ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$), are unreactive toward olefins.[335,336] New advances on bis(imino)pyridine Co catalysts **138** will be discussed in the following section.

Substitution of the central pyridine donor for a pyrimidine ring (**133e**) results in a slight reduction of activity and the formation of polymer with narrower polydispersity and an increased proportion of unsaturated end groups.[330,353] A different class of complex is obtained when the ring size of the central donor is changed to a five-membered pyrrole ring, as shown in the bis(imino)pyrrolide-based complex **133h**.[162,366] The smaller "reach" of the pyrrolide-based ligand leads to bidentate coordination of two ligands to one metal center being preferred, as observed for the complexes of Cr[290] and Fe.[162] Complexes with thiophene- and furan-based ligands (**133f**[358] and **133g**[365]), with moderate to low ethylene polymerization activity, have been disclosed in the patent literature. However, the coordination mode of the ligand and the oxidation state of the metal remain unclear, and attempts to isolate Fe^{II} and Co^{II} complexes with these ligands were unsuccessful.[330]

The nature of the pendant imino donor also influences to a great extent polymerization activity and polymer properties. Fe-based aldimine complexes **133k** generally show an order of magnitude lower activity than their ketimine counterparts derived from 2,6-diacetylpyridine[312] and 2,6-dibenzoylpyridine.[330,369] The acidity of the ketimine proton in **133** can also be exploited to prepare new ketimine ligands with increased steric bulk at the imine carbon, e.g., **133i** with $R/R' = H$, Me or $R = CH_2Ph$, affording highly active polymerization catalysts.[352] Herrmann and co-workers utilized a similar synthetic route to introduce anchoring groups for the heterogenization of the catalyst on silica.[342] The imine moiety can also be substituted by heteroatom-containing groups via nucleophilic attack on imidoyl chloride intermediates. In this fashion N-, O-, and S-substituted imines of general structure **133j** (R = aryl, alkyl) have been prepared.[329,354] They are also highly active ethylene polymerization catalysts, S-substituted complexes being generally more active than their O- and N-substituted analogues. Only low to moderate ethylene polymerization activities were observed when one or both imino functions were replaced by neutral amino donors (**133l**).[326] The tetrahedral amino donor affords a different orientation of the aryl substituents as compared to the bis(imino)pyridine complex, which might lead to more hindered access of the monomer and hence lower activity. Electronic factors might also be significant, since ligand-based radical anions stabilized by an extended π-conjugated system through the ligand backbone have been observed for bis-

(imino)pyridine ligands and may be present in the active species formed after addition of the cocatalyst.[324,370,371] The same argument may explain the reluctance of bis(iminophosphinimine)pyridine Fe complexes of the type **133m** to polymerize ethylene, although under certain high-pressure conditions some polymer can be obtained.[265,338] A reduced reactivity toward ethylene is also observed when one imino moiety is replaced by a pyridine ring (**133o**). The resulting imino-bipyridine ligand gives much less steric protection to the metal center and leads to an increased rate of chain termination by β-hydrogen transfer, resulting in the formation of low-molecular-weight oligomers.[328] Bis(oxazoline)pyridine complexes of Ru and Fe (**133q**) were reported by Nomura and co-workers, and only trace amounts of polymer were obtained.[339,340] Complexes with a variety of different aryl-imino substituents have also been reported, but they generally exhibit lower activities than the parent complex **133a**.[332−334] Bis(hydrazone)pyridine complexes of the types **133n** and **133p**[325,359−361] afford a mixture of low-molecular-weight polymer and oligomers with moderate catalyst activities. The related pyrrolyl derivative **133n** is highly active and produces only solid polymer though the catalyst lifetime, and the PE molecular weight is considerably lower than that for **133a**. This illustrates that the size and shape of the imino-substituents in **133** are not the only factors controlling activity and molecular weight; electronic effects also clearly play a role.

Propylene polymerization by bis(imino)pyridine iron complexes has also been investigated.[359,362,372,373] Small and Brookhart studied a number of bis(imino)pyridine complexes of iron and reported activities for propylene polymerization up to 950 g mmol^{-1} h^{-1} bar^{-1} at −20 °C.[372] The polymerization proceeds with high regioregularity via a 2,1-insertion mechanism, affording low-molecular-weight polymer (M_n up to 6500). Remarkably, the polymer exhibits enriched isotacticity with [mm]-diad values of up to 67%, governed by a chain-end control mechanism. Reduction of the steric bulk on the aryl-imino substituents leads to a head-to-head dimerization of α-olefins.[374] The copolymerization of ethylene with higher α-olefins has also been investigated, but α-olefin incorporation is generally very low.[308,357−359]

B. Anionic Ligands

As outlined in the previous section, structural modifications to the bis(imino)pyridine ligand generally lead to lower activities, indicating that this ligand framework is rather unique in its ability to stabilize highly active ethylene polymerization catalysts of iron. Many attempts have been made to extend the ligand family to anionic derivatives, such as those shown in Figure 24. However, **134**,[287,375] **135**,[287,376] and **136**[377] (Figure 24) generally afford only low ethylene polymerization activities. Stephan and co-workers expanded the chemistry of bulky phosphinimide ligands in ethylene polymerization catalysis to Group 8 metals and prepared the binuclear Fe^{III} complex **137**.[378] It shows an activity of 55 g mmol^{-1} h^{-1} bar^{-1} and produces high-molecular-weight PE with a narrow molecular weight distribution.

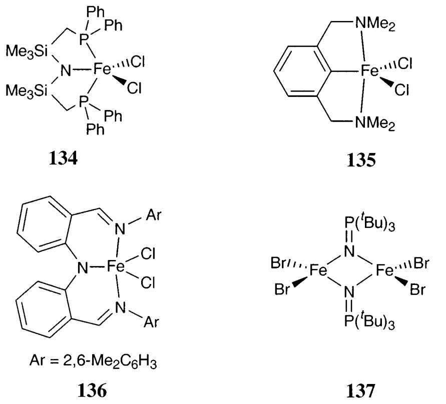


Figure 24. Fe^{III} precatalysts with anionic nitrogen- and carbon-based donors.

IX. Group 9 Catalysts

New advances in olefin polymerization catalysis using cobalt complexes have been based mainly around the bis(imino)pyridine ligand framework (**138**, Figure 25). These ligands promote the highest activities for cobalt centers reported to date, although in general their activities are an order of magnitude lower than those for their iron relatives. Structural modifications, as outlined in the previous section (see Table 1), for the Fe-based catalysts have in most cases also been applied to the Co complexes, and generally similar activity trends for ethylene polymerization are observed. As for the iron system, deviations away from the bis(imino)pyridine ligand frame generally afford dramatic lowering of activities. For example, complexes bearing bis(phosphinimide)pyridine (**139**)[265,338] and imino-pyrrolide ligands (**140**)[162] exhibit only moderate activities for the polymerization and oligomerization of ethylene, respectively. The analogous Fe complexes bearing bis(phosphinimide)pyridine (**133m**) and bis(imino)pyrrolide (**133h**) ligands are unreactive toward ethylene.

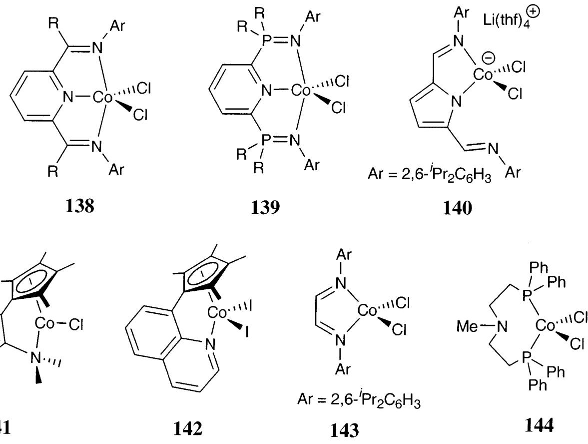
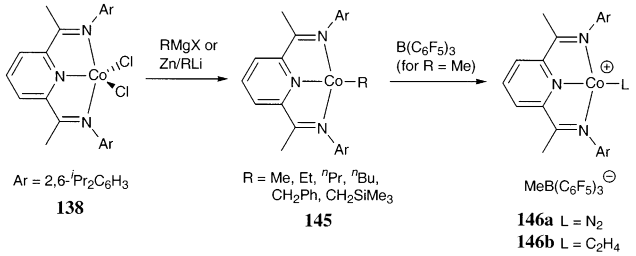


Figure 25. Co-based precatalysts.

For the bridged Cp-amine Co^{II} and Co^{III} complexes **141** and **142**, low ethylene polymerization activities are observed, by contrast to the Cr^{III} system, **112**, bearing the same ligand.[276,379] A remarkable difference in activity and polymer properties is also observed for the α-diimine Co complex **143** in comparison to the analogous Ni complex. After activation with MAO, **143** produces mainly branched oligomeric oils from ethylene with an activity of up to 340 g mmol^{-1} h^{-1} bar^{-1}, whereas the related α-diimine Ni complex forms high-molecular-weight PE at a rate an order of magnitude higher.[380,381] The tetrahedral diphosphine Co complex **144** exhibits, like its Fe counterpart, only low ethylene oligomerization activity.[382]

The nature of the active species in the bis(imino)pyridine Co system **138** has been investigated. Computational studies were carried out on **138**, where a cationic Co^{II} alkyl complex was presumed to be the catalytically active species.[383] However, subsequent experimental results have implicated Co^{I} or Co^{III} centers in the active site.[384,385] Addition of excess MAO to **138** results in a color change from green to purple.[312] The same purple coloration is observed for diamagnetic Co^{I} alkyl complexes of the type **145**, which can be obtained from **138** by direct reductive alkylation using Grignard reagents or by reduction of **138** by Zn to yield a (bis(imino)pyridine)Co^{I}Cl complex, followed by alkylation using alkyllithium reagents (Scheme 2). Complexes of the type **145** do not polymerize ethylene by themselves, but after addition of excess MAO, PE is produced with properties identical to, and with activity similar to, those of MAO-activated **138**, implying the presence of the same active species. Addition of $B(C_6F_5)_3$ to the methyl complex **145** under a nitrogen atmosphere results in the formation of the cationic Co^{I} dinitrogen complex **146a**, which has been structurally characterized.[384] Addition of ethylene to **146a** results in the slow formation of PE. Once the excess ethylene has been consumed, the cationic ethylene complex **146b** remains in solution. These observations indicate the formation of a bis(imino)pyridine Co^{I} alkyl complex of the type **145** after addition of MAO to **138**, followed by alkyl abstraction to a cationic complex of the type **146** with a MAO-based counterion. A number of pathways for the initiation of the polymerization reaction from such a cation containing *no* Co-alkyl groups are possible; all appear to involve oxidation of the metal center to Co^{III}.[385]

Scheme 2. Reductive Alkylation and Formation of Cationic Bis(imino)pyridine Co Complexes



X. Group 10 Catalysts

A. Neutral Ligands

1. α-Diimine and Related Ligands

The family of cationic α-diimine Ni and Pd catalysts of the type **147** (Figure 26), introduced by Brookhart and co-workers,[8] has continued to attract much interest. The steric and electronic properties of the α-diimine ligand can be readily adjusted by modifying the imino carbon and nitrogen substituents, and hence a large number of structural variations have been reported in the academic and patent literature. Advances up to the year 2000 have been reviewed by Ittel et al.[386] and will not be discussed here in any detail. In more recent work, Gottfried and Brookhart have reported the living polymerization of ethylene using single-component Pd catalysts of the type **147** at 5 °C and 100−400 psi ethylene pressure.[387] The combination of low temperature and high pressure leads to improved catalyst stability and initiation rate; thus, polydispersities ca. 1.05 with a linear increase of M_n over time can be obtained. This illustrates the pronounced effects of polymerization conditions on the catalyst performance and resultant polymer properties, as reported by a number of groups.[388−396] In addition to previously published insights into the polymerization mechanism,[386,397] a number of spectroscopic[317,318,398−401] and computational[402−409] studies have been carried out and, in general, have provided further confirmation that a cationic alkyl ethylene complex is the resting state of the catalyst system. The formation of highly branched polymer is the result of a series of β-hydrogen elimination/re-insertion reactions via the β-agostic cationic alkyl intermediate.

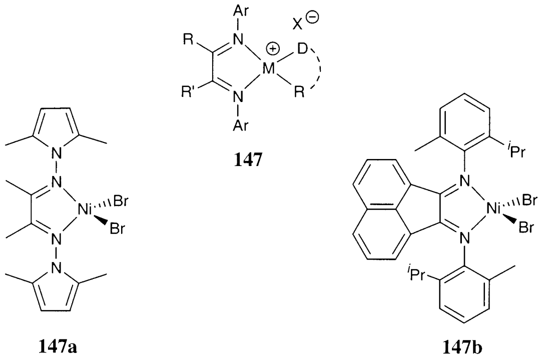


Figure 26. Ni and Pd α-diimine precatalysts.

A different mode of precatalyst activation was studied by Erker and co-workers, who isolated and structurally characterized a zwitterionic α-diimine Ni complex derived from the reaction of (α-diimine)Ni-(η^4-butadiene) with $B(C_6F_5)_3$; this gave an ethylene polymerization activity of 80 g mmol^{-1} h^{-1} bar^{-1} in the absence of cocatalyst.[410] A series of ligand modifications has been disclosed by Eastman Chemical Co. in which N-pyrrolyl substituents provide the steric protection to the metal centers needed to reduce β-hydrogen chain-transfer rates (see also the bis(imino)pyridine Fe complex, **133n**, in Table 1).[360,361] Ethylene polymerization activities of up to 5800 g mmol^{-1} h^{-1} bar^{-1} can be achieved with complex **147a**, which is in the same range as for related imino-aryl derivatives under similar conditions.[8]

Brookhart[8] and Pellecchia[411] and their co-workers have also investigated the ability of α-diimine Ni and Pd catalysts to polymerize α-olefins. At low temperature, propylene polymerization using Ni-based catalysts is living[412] and largely syndiotactic, arising from a chain-end-controlled mechanism.[413] Since the resultant polymers are amorphous elastomers, efforts have been undertaken by a number of groups to prepare C_2-symmetric α-diimine Ni and Pd complexes in order to access isotactic PP through an enantiomorphic site control mechanism.[414,415] Results with ligands bearing imino-aryl groups containing two different ortho substituents in C_2-symmetric complexes (**147b**) suggest that both mechanisms are operative simultaneously, resulting in reduced syndiotacticity of the polymer compared with that of symmetrical α-diimine complexes.[416]

The copolymerization of ethylene with acrylates at high temperature and pressure has been reported using cationic α-diimine Ni allyl complexes of the type **147** in combination with $B(C_6F_5)_3$ activator;[417,418] the temperature/pressure regime is considerably higher than that used for earlier copolymerization studies using α-diimine Pd complexes and generally affords superior comonomer incorporation.[419−421] The copolymerization of ethylene with other polar vinyl monmers has also been investigated.[43,422−424]

The α-diimine Ni and Pd catalysts have also found successful applications in reactor blending experiments with early transition metal catalysts to afford polymers with novel microstructures and properties.[347,425−427] Ethylene polymerization reactions can also be carried out in biphasic toluene/ionic liquid media[428] or in water,[429] but activities are reduced to moderate to very low levels, respectively, as compared to those found for reactions carried out in more conventional organic solvents. Due to the low solubility of ethylene in water, olefin coordination becomes the rate-determining step at pressures below 20 bar. The amorphous, rubbery polymers obtained in the aqueous phase with Pd complexes of the type **147** generally show a lower degree of branching and higher molecular weight compared to those of reactions carried out in organic solvents.[430]

2. Other Neutral Nitrogen-Based Ligands

As outlined in the previous section, steric protection of the axial positions in the square-planar active species in catalysts of the type **147** is essential for retarding associative chain displacement reactions. When sterically less demanding aryl substituents are employed, β-hydrogen elimination, followed by fast olefin displacement, leads to the formation of α-olefins.[431] Similar observations have been made for the pyridine-based ligands depicted in Figure 27. Several groups have described neutral and cationic Ni and Pd complexes with unsymmetrical imino-pyridine ligands (**148**), and generally greatly reduced ethylene polymerization activities and reduced molecular weights are obtained.[432−437] The absence of any significant steric protection in catalysts **149**/MMAO (with R = R′ = H),[431] **150**/$Et_3Al_2Cl_3$,[438] and **151**/MAO[439] leads to the formation of α-olefins, though some substituted bipyridine complexes of the type **149**[440] (with R, R′ ≠ H) also gave small amounts of solid polymer. Exclusive formation of low-molecular-weight α-olefins with high activity is observed for Ni complexes bearing neutral 2,6-bis(imino)phenol ligands.[441]

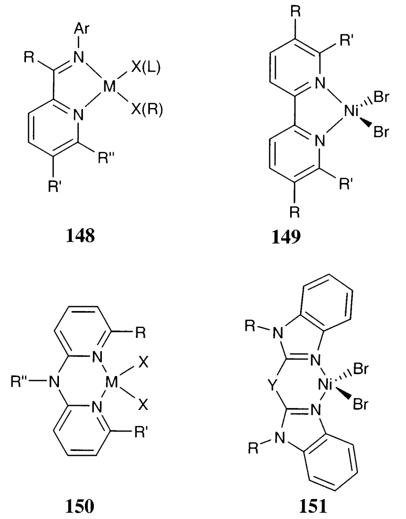


Figure 27. Group 10 metal precatalysts with neutral nitrogen-based donors.

3. Chelating Phosphorus-Based Ligands

There is a rich coordination chemistry of phosphine ligands with late transition metals, but the strong σ-donor capacity of these ligands had been presumed to be more suited to catalytic reactions requiring nucleophilic metal centers.[442] This appears to be supported by the low ethylene polymerization activity observed for the diphosphinidine complex **152** ($[H(OEt)_2][B(Ar^F)_4]$ activation), which is sterically similar to α-diimine complexes, and suggests that the polymerization activities in these Group 10 metal systems are strongly dependent upon the nature of the donor atom.[443] Low ethylene polymerization activity has also been reported for Ni complexes bearing neutral imino-phosphine ligands.[444] However, surprisingly high ethylene polymerization activities of up to 2200 g $mmol^{-1}$ h^{-1} have been observed by Pringle, Wass, and co-workers for the phosphine-based complex **153** (Figure 28).[445] The catalyst exhibits a zero-order dependence on ethylene pressure and produces high-molecular-weight polymer. Simi-

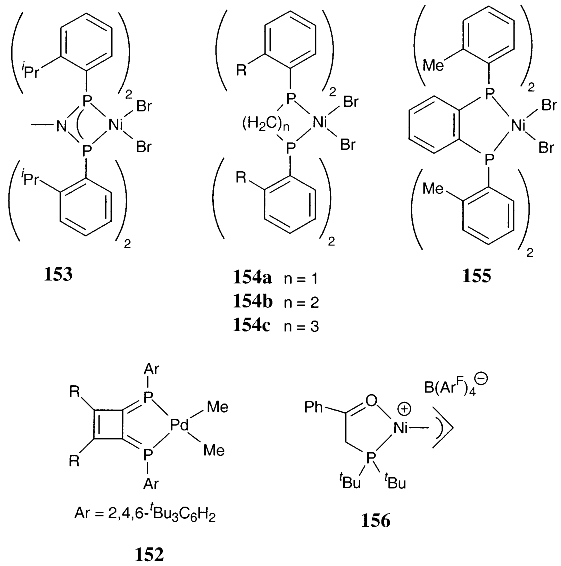


Figure 28. Group 10 metal precatalysts with neutral phosphorus-based donors.

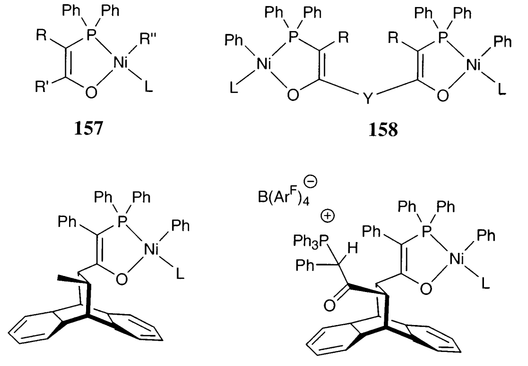
lar to α-diimine complexes, reducing the size of the arylphosphine substituents leads to reduced activity and lower molecular weight polymer. Substitution of the ligand NMe backbone for a CH_2 unit (**154a**) results in increased activity, but a higher rate of *β*-elimination leads to the formation of low-molecular-weight, highly branched PE. The less rigid ethyl- and propyl-bridged diphosphine complexes **154b**,**c** are unreactive toward ethylene,[446] whereas the phenylene derivative **155** is again active, suggesting that backbone rigidity has a significant influence on catalyst activity.

Brookhart and co-workers have reported ethylene polymerization activities up to 700 g $mmol^{-1}$ h^{-1} bar^{-1} using the single-component Ni catalyst **156**, which bears a neutral [PO] ligand.[447] Linear PE with M_w of ca. 10 000 and a molecular weight distribution between 2.1 and 2.7 is obtained. The analogous Pd complexes are an order of magnitude lower in activity, and the molecular weight of the polymer is also greatly reduced. Complex **156** has also been shown to copolymerize ethylene with methyl-10-undecenoate, albeit with greatly reduced activity; up to 6.6 mol % incorporation of the polar monomer can be obtained.

B. Monoanionic Ligands

1. [PO] Chelates

Monoanionic [PO] ligands on Group 10 metals lead to formally neutral catalysts and have been extensively studied as part of the Shell Higher Olefin Process (SHOP) for ethylene oligomerization. Depending on the reaction conditions, solid PE can also be obtained with complexes of the general structure **157** (Figure 29).[448,449] The precatalysts can be activated by treatment with a suitable reagent to abstract the donor group L (e.g., $Ni(COD)_2$ or $B(C_6F_5)_3$ for L = PPh_3), but active catalysts can also be conveniently accessed in situ by treatment of a suitable Ni(0) precursor such as $Ni(COD)_2$ with the α-keto-ylide ligand precursor. Certain donors such as pyridine do not require an abstracting agent.



157 **158** **159** **160**

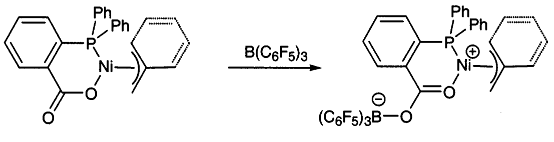
Figure 29. Ni complexes bearing monanionic [PO] ligands.

Ethylene polymerization activities up to ca. 5300 g $mmol^{-1}$ h^{-1} bar^{-1} have been reported for Ni complexes **157** containing fluorinated substituents (R = COOR, R′ = CF_3, C_3F_7 or C_6F_5), substantially higher than for their hydrocarbon counterparts.[450] The polymer is highly linear (M_w ca. 4000), with a narrow molecular weight distribution. The size of the ester substituent was found to have little effect on activity or molecular weight in this system. The reduced sensitivity of these neutral catalysts toward polar functional groups is demonstrated by their ability to polymerize olefins in the presence of water. Homo- and copolymerizations of ethylene and α-olefins using complexes **157**,[429,451] as well as the binuclear complexes **158**,[452] have been studied in aqueous emulsion and water as the reaction media. The emulsion polymerization activity is reduced by 2 orders of magnitude, but stable polymer lattices, especially from the copolymerization reactions, can be obtained.[453] Catalytic aqueous polymerization has been reviewed recently.[454]

Gibson and co-workers have shown that very bulky groups positioned adjacent to the oxygen donor afford dramatic increases in activity, believed to be a result of steric protection of the relatively exposed O-donor atom. For example, **159** gives an activity of 1730 g $mmol^{-1}$ h^{-1}, while the sterically more protected derivative **160** affords an activity of 34 880 g $mmol^{-1}$ h^{-1} (employing $Ni(COD)_2$ as phosphine scavenger).[455] The latter is several orders of magnitude higher than that for the less bulky complex of the type **157** (with R = R′ = Ph). However, the polymer properties are independent of the nature of the substituent adjacent to the oxygen donor: in all cases, linear PE with M_n in the range of 5000−10 000 and with narrow molecular weight distributions (2.0−3.7) is obtained. Complexes of types **159** and **160** are capable of copolymerizing ethylene with methyl methacrylate (MMA) to give MMA-end-functionalized PE, consistent with a polymerization mechanism involving insertion of MMA into the growing PE chain, followed immediately by chain termination via *β*-hydrogen transfer.[456] The copolymerization of ethylene with methylacrylate (MA) to give MA incorporated into the PE chain has more recently been reported using a phosphino-sulfonate Pd complex.[457]

A novel approach to transforming a neutral Ni catalyst into a more electron-deficient cationic species has been reported by Bazan and co-workers (Scheme 3). Addition of $B(C_6F_5)_3$ to the phosphino-carboxylate Ni complex, **161**,[458] results in the formation of the cationic species **162** via coordination of $B(C_6F_5)_3$ to the carbonyl oxygen of the carboxylate unit.[459] The cationic derivatives afford higher ethylene oligomerization activities than their neutral counterparts, 1-butene being formed predominantly in all cases.[460] Dual-catalyst blending experiments combining these Ni systems with early transition metal catalysts capable of incorporating α-olefins into the growing polymer lead to the formation of branched PEs.[459,461] The rate-enhancing effect of $B(C_6F_5)_3$ for the poly-

Scheme 3. Borane Activation of [PO]Ni(allyl) Complexes

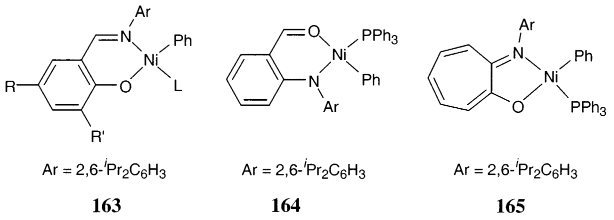


161 **162**

merization of ethylene has also been observed in (α-imino)-,[462] (pyridine)-carboxamidate,[463] iminocarboxylate,[464] and α-iminoenamide[465] systems.

2. [NO] Chelates

A series of salicylaldiminato complexes of Ni (**163**, Figure 30), bearing bulky imino substituents, have been reported by Grubbs and co-workers.[466] The bulky groups retard associative displacement reactions in much the same way as for cationic Ni(α-diimine) systems. Computational studies also suggest that sterically demanding *o*-phenoxy substituents promote the dissociation of the donor group L (PPh_3, MeCN) in the initiation process.[467] The formation of inactive bis-ligand complexes is also prevented. Thus, a pronounced dependence of activity on R′ is observed, and the catalyst activity, as well as molecular weight and linearity, increases in the order ^{t}Bu < Ph < 9-phenanthrenyl < 9-anthracenyl, after activation of **163** (L = PPh_3) by $Ni(COD)_2$. The highest activity, of several hundred g $mmol^{-1}$ h^{-1} bar^{-1}, is observed with complexes containing a weakly coordinating acetonitrile ligand L.[468] This family of neutral Ni catalysts also exhibits good functional group tolerance and remains active in the presence of polar or protic solvents.[469,470] It also incorporates substituted norbornenes and α,*ω*-functionalized olefins.[468,471,472] The binding of polar monomers by **163** through a *π*-complex is calculated to be preferred over the O- or N-complexed species.[405,473,474] Derivatives bearing vinyl-substituted aryl groups have been utilized to immobilize the catalysts.[475] Novak and co-workers recently reported a single-component Ni catalyst, **164,** bearing an amido-aldehyde [NO] ligand for the polymerization of ethylene with similar activities to **163**.[476] Ethylene oligomerization using a number of neutral Ni complexes bearing anionic [NO] and [OO] chelate ligands has been studied by Carlini and co-workers, and generally low to moderate activities were obtained at elevated pressure.[477−480]



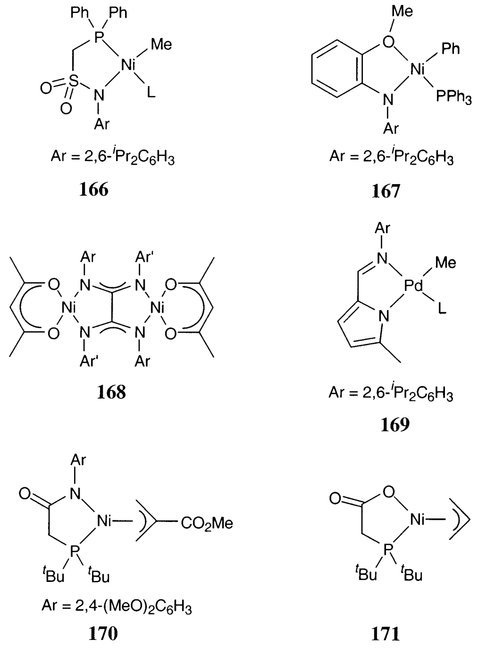
163 **164** **165**

Figure 30. Ni precatalysts bearing monoaniomic [NO] ligands.

A neutral Ni catalyst based on an anilinotropone ligand, forming a five-membered chelate, has been reported by Brookhart and co-workers (**165**).[481] No phosphine scavenger is required, and **165** produces high-molecular-weight PE with moderate activitiy. Polydispersities are in the range 1.75−2.03 and are independent of the reaction conditions, whereas the branching number decreases, and the molecular weight increases, with pressure. The catalytic activity is reduced only by a factor of 3.5 in the presence of water.

3. Other Monoanionic Ligands

A number of other neutral catalysts have been reported and are summarized in Figure 31. Single-component phosphinosulfonamide Ni catalysts of the type shown in **166**, even with bulky aryl substituents, do not polymerize ethylene, but branched oligomers are produced with moderate activities.[482] The ethylene oligomerization activity for the related five-membered [NO] chelate **167** in combination with $B(C_6F_5)_3$ is low.[483] Steric protection of the metal center deriving from both donors can be provided by the oxalaldiminato ligand (**168**). Less bulky aryl substituents such as *o*-tolyl lead to the formation of α-olefins exclusively, whereas solid PE is obtained for Ar = Ar′ = mesityl, though with low activity.[484,485] Novak and co-workers have described a series of imino-pyrrolide Pd complexes (**169**), which are unreactive toward ethylene but produce acrylate-rich 1-hexene-methylacrylate copolymer.[486] However, a radical rather than coordinative polymerization mechanism was found to be operative. Ethylene/acrylate copolymers have been obtained with very low activities using complexes **170** and **171** in combination with a suitable Lewis acid, such as $B(C_6F_5)_3$, and using related neutral [PN], [PO], and [NO] Ni allyl complexes.[487−490]

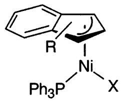


166 **167** **168** **169** **170** **171**

Figure 31. Ni precatalysts bearing other monoanionic ligands.

4. Carbon-Based Ligands

Longo and co-workers have shown that simple nickelocene complexes such as Cp_2Ni and $Cp^*{}_2Ni$ can polymerize ethylene with moderate activities upon activation with MAO.[491] Collins, Zargarian, and co-workers have reported activities of up to 130 g $mmol^{-1}$ h^{-1} bar^{-1} with neutral Ni catalysts bearing substituted η^3-coordinated indenyl ligands (**172**, Figure 32) after activation with MAO. The phosphine ligand remains attached to the metal center in the active species, and high-molecular-weight PE is formed. However, the majority of the consumed ethylene is dimerized by a mechanism involving cationic intermediates.[492]



172

Figure 32. Ni precatalysts bearing a carbon-based ligands.

XI. Group 11 Catalysts

To date, reports on olefin polymerization catalysts based on copper are scarce. The benzamidinate complex **173**[493] and the benzimidazole complexes of the type **174**[494,495] (Figure 33) both show low ethylene polymerization activities. Catalysts **174** are also able to produce acrylate-rich ethylene–acrylate copolymers with very low activities.[495,496] The α-diimine Cu^{II} complex **175** produces very high-molecular-weight PE with moderate activity.[497] Stabilization of the active species through weak interactions with the *o*-phenyl groups of the ligand seems to contribute to the catalyst's stability, since only trace amounts of polymer are obtained with ligands bearing isopropyl substituents in this position. The beneficial effect of *o*-phenyl substituents has also been noted for related Ni catalysts.[498]

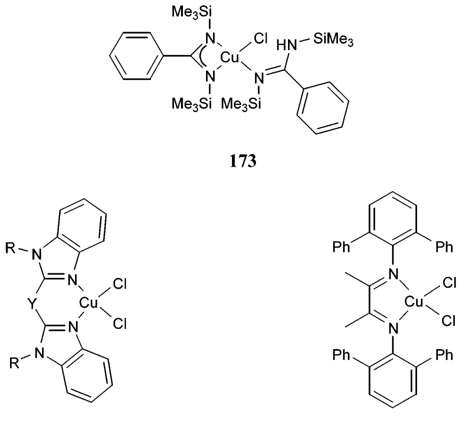
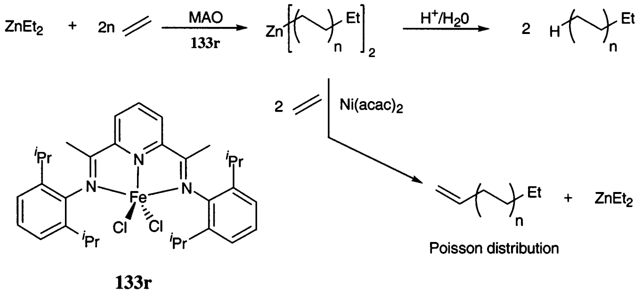


Figure 33. Group 11 metal precatalysts.

XII. Group 12 Catalysts

Although there have been no reports of single-site olefin polymerization catalysts based on Group 12 metals, it has recently been shown that transition metal catalysts, such as **133**, can catalyze PE chain growth on zinc centers, affording linear alkanes or α-olefins with a Poisson distribution.[499] In the polymerization of ethylene using complexes **133** and MAO as cocatalyst, both *β*-hydrogen transfer and chain transfer to aluminum are operative as chain-termination processes, the latter leading to fully saturated low-molecular-weight PE.[312] As outlined in Scheme 4, addition of excess $ZnEt_2$ to the **133r**/MAO system leads to a very fast and reversible chain transfer of the polymer chain between iron and zinc, resulting in the formation of long-chain dialkyl zinc species. Displacement of the alkyl chains from zinc can be achieved by a displacement reaction catalyzed by $Ni(acac)_2$ in the presence of ethylene. Under these circumstances, linear α-olefins are obtained with a Poisson distribution of chain lengths.

Scheme 4. Catalyzed Chain Growth on Zn



XIII. Group 13 Catalysts

The polymerization of ethylene with transition-metal-free homogeneous Al catalysts has attracted attention in recent years, and several new catalysts have been added to the family of mono- and bis(amidinate) complexes reported by Jordan, Teuben, and their co-workers.[500–502] Activation of the Al complexes depicted in Figure 34 is generally achieved by conversion of the dialkyl precursor into a cationic alkyl species using a suitable Lewis acid such as $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$. Low polymerization activities (up to 3 g mmol^{-1} h^{-1} bar^{-1}) and the formation of high-molecular-weight PE with narrow polydispersities were reported for the Al precatalysts **176**[501] and **177**.[503,504] Higher activities (up to 120 g mmol^{-1} h^{-1} bar^{-1}) and lower molecular weight polymer (M_n = 2400–7800) were found for complexes **178**, which are obtained via the reaction of $AlMe_3$ with the bis(imino)pyridine ligand, resulting in methyl migration from Al to the imino carbon.[505] Neutral and cationic salicylaldiminato complexes of types **179**[506] and **180**[507] have also been investigated, but their ethylene polymerization activity is very low.[508] Sen and co-workers were able to homo- and copolymerize

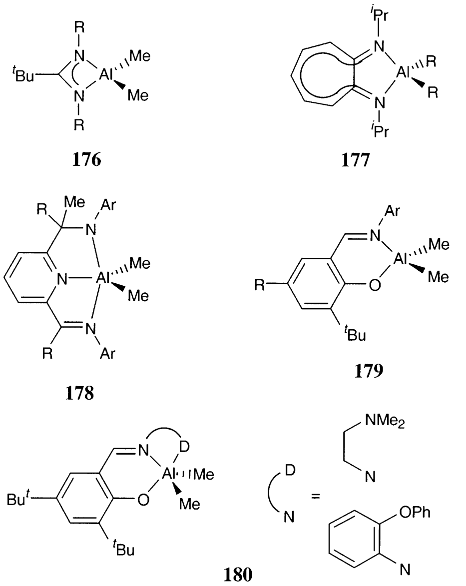


Figure 34. Al-based precatalysts.

ethylene and propylene with very low activity using mixtures of $AlEt_3$ or $AlMe_3$ and $B(C_6F_5)_3$.[509]

Although cationic alkyl complexes derived from **176**−**180** could be isolated and characterized, it remains largely unclear if they are the active species in these systems. Recent structural data obtained for the reaction products of **176** with Lewis acids indicate the formation of complex cationic species.[510] Computational studies also suggest that the activation barriers for β-hydride elimination are lower than those for ethylene insertion for simple cationic alkyl complexes derived from **176**−**178**, and more complex structures for the active species may have to be considered.[511−513]

XIV. Summary and Outlook

The past 4 years have seen a phenomenal growth in research activity in the field of metal-catalyzed olefin oligomerization and polymerization, with many new systems being described. The drive has continued toward greater control over the polymer product and, by implication, the way in which metals with their attendant ligands control the chain growth process. The selection of metal−ligand combinations suitable for stabilizing polymerization-active centers has been at the heart of the discovery process, and one of the most noteworthy advances in this regard has been the increased prominence of late transition metal systems. For example, the number of reports on nickel catalyst systems through the period 1998−2001 has exceeded those for titanium during the previous 4-year period, while catalysts based on iron have featured strongly, and systems based on copper have started to emerge. With a role for zinc in catalyzed chain growth, the only first-row transition metal so far not to have found an active role in olefin polymerization is manganese. Through judicious ligand selection, there is no reason to suspect that this situation will not be rectified before too long.

At the same time as the discovery of new catalysts, it should also be noted that there have been equally significant advances in process design and the engineering of products derived from single-site catalysts. Although it has not been within the scope of this review to address these developments here, they are especially important for bringing new polyolefin products closer to the market place. Undoubtedly, non-metallocene polymerization catalysts have provided many additional options, if also a few more challenges, for industry.

Perhaps one of the most significant advances in our understanding of the factors responsible for stabilizing active catalysts during the period 1994−1997 was the recognition that bulky substituents can play a crucial role, not only in stabilizing the active site, but also in controlling chain-transfer processes. However, during the past 4 years or so, highly active systems based on ligands bearing relatively small substituents have also been discovered, for example, bis-ligand Ti systems (**72**) and mono-chelate Cr systems (**125**). These developments highlight that small substituents can be advantageous in certain situations, e.g., where two chelate ligands are to be accommodated around a metal center, or if the metal coordination geometry is, for example, other than square planar, and serve to emphasize that there is no single rule for ligand selection that is applicable to all metals. Preferred coordination numbers and geometries, characteristic of a particular metal, have to be given due consideration.

While it is now possible to design active catalyst systems, and even address aspects of selectivity in a general sense (oligomers vs polymer, linear vs branched PE, tacticity, etc.), it is still not possible to predict with any degree of certainty the maximum activity or lifetimes achievable for a new catalyst system, nor the finer details of product selectivity. This has seen the increasing adoption of high-throughput screening (HTS) methodologies, which are likely to be an important growth area in the coming years, especially for industrial research laboratories. Primary HTS protocols allow diverse areas of metal−ligand space to be explored and evaluated in a short period of time, while a more in-depth evaluation of reaction parameters (a secondary screen) provides a vehicle for obtaining a swift understanding of catalyst performance, structure−activity relationships, and substrate/product selectivities. The usefulness of HTS methodology is, however, dependent upon high-quality targeted library design, coupled with robust quality experimentation. When these come together, the discovery, evaluation, and development process may have a few more gears to step up.

XV. Glossary

Ar	aryl
Ar^F	$3,5-(CF_3)_2C_6H_3$
CGC	constrained geometry catalyst
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
D	generic neutral donor group
EPR	electron paramagnetic resonance
Et	ethyl
HTS	high-throughput screening
^{i}Bu	isobutyl
^{i}Pr	isopropyl
L	generic neutral ligand
MAO	methylaluminoxane
Me	methyl
MeCN	acetonitrile
MMAO	modified methylaluminoxane
M_n	number-average molecular weight
M_w	weight-average molecular weight
PDI	polydispersity index
PE	polyethylene
Ph	phenyl
PP	polypropylene
py	pyridine
SHOP	shell higher olefin process
^{t}Bu	*tert*-butyl
thf	tetrahydrofuran
TMA	trimethylaluminum
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
X	generic anionic ligand

XVI. References

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