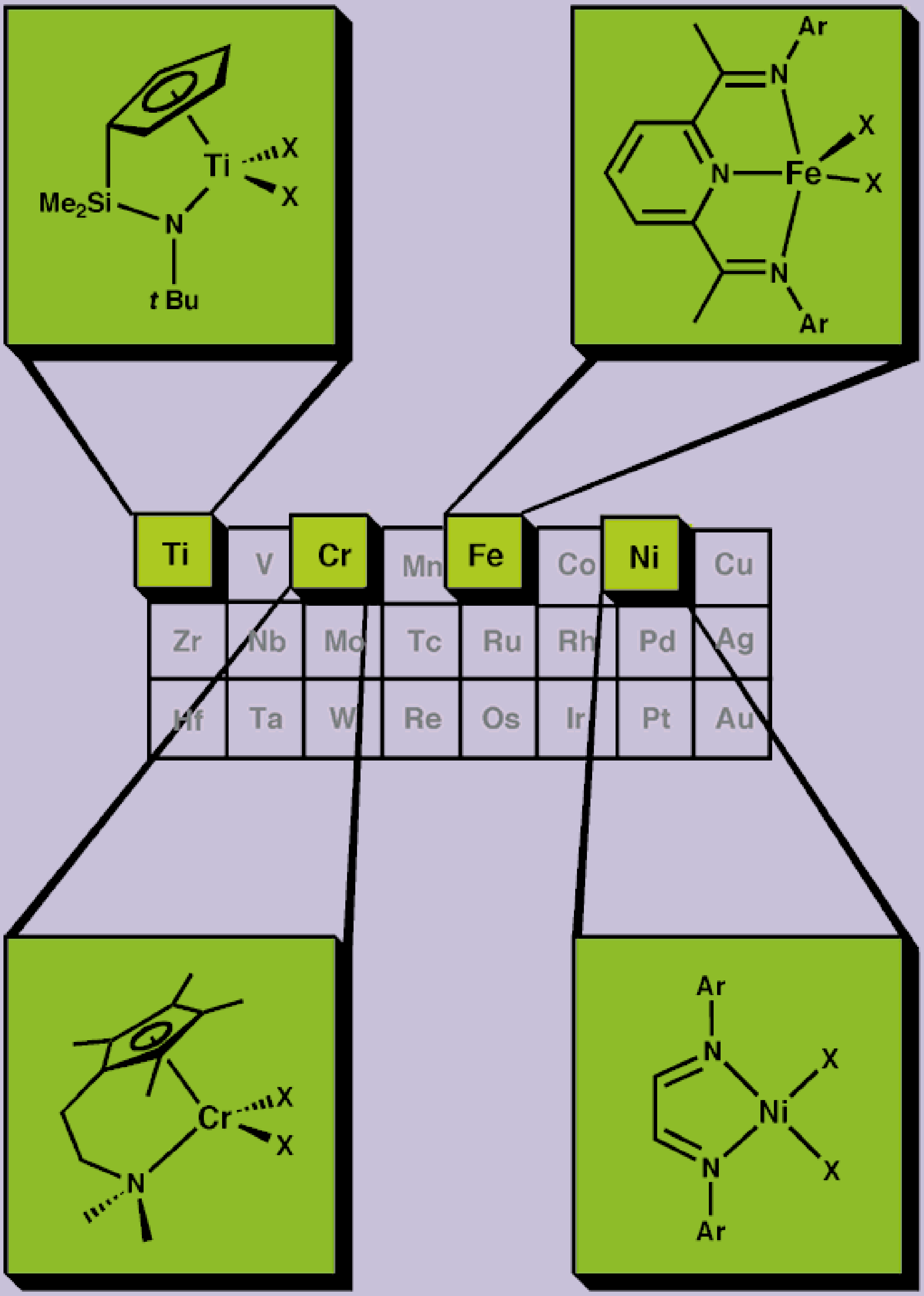
Examples of highly active non-metallocene olefin polymerization catalysts across the transition series



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The Search for New-Generation Olefin Polymerization Catalysts: Life beyond Metallocenes

George J. P. Britovsek, Vernon C. Gibson,* and Duncan F. Wass

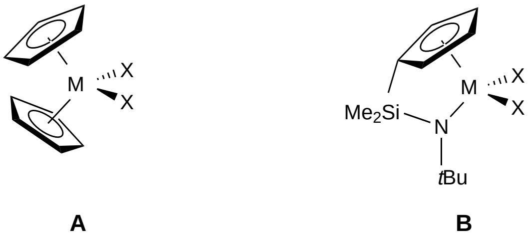
The introduction of well-defined, single-site organotransition metal olefin polymerization catalysts in the early 1980s highlighted the possibilities for controlling and dramatically improving the properties of commodity polymer products such as polyethylene and polypropylene. Group 4 metallocenes and half-sandwich titanium–amide complexes (constrained-geometry catalysts) have been at the forefront of these developments, and, as we approach the late 1990s, these catalysts are increasingly finding their way into commercial operations. However, it is generally acknowledged that no single class of catalyst will be capable of controlling all of the macromolecular parameters relevant to a wide and varied range of polyolefinic products. Over the past few years, an intense search has therefore developed, in both academic and industrial research laboratories, for new-generation catalysts. Some of the most significant recent developments have occurred with late transition metal systems. Particularly, the discovery of exceptionally active catalysts based on iron, a metal that had no previous track record of being applied in this way, has signposted the way for further technologically significant advances in the field. In this review, we highlight the key advances that have occurred in the discovery and development of non-Group 4 metallocene catalysts, amply demonstrating that there are significant signs of life beyond the Group 4 metallocenes.

Keywords: homogeneous catalysis · olefins · polymerizations · transition metals

1. Introduction

1.1. Background

The past 15 years have witnessed tremendous advances in the design and application of organometallic complexes as α-olefin polymerization catalysts; many are now reaching the early stages of commercialization. These developments have grown out of an increased understanding of the factors that are important for stabilizing polymerization-active metal centers and controlling their activity and selectivity, combined with the industrially important discovery that methylalumoxane (MAO) cocatalysts afford highly active and long-lived catalyst systems. To date, Group 4 metallocenes (**A**, Scheme 1) and related catalyst systems such as the half-sandwich amide or constrained-geometry catalysts (**B**) have been at the forefront of these developments.



Scheme 1. Group 4 metallocenes (**A**) and constrained-geometry catalysts (**B**).

However, the search for new catalysts would appear to be far from over. Driven by industry's desire to obtain ever greater control over the properties of the resultant polymers and to extend the family of products to new monomer combinations, the search is gathering apace for yet new highly active, selective catalyst families that tolerate a variety of functional groups. In this review we shall highlight recent advances in the search for new catalysts, focusing primarily on ligand–metal complex design and catalyst activity rather than the properties of the resultant polymeric materials. A simple classification scheme is outlined that allows ligand–metal combinations for active catalysts to be charted. Variations on Group 4 metallocene catalyst systems will not be discussed in any detail here since they have been reviewed extensively elsewhere.[1–7]

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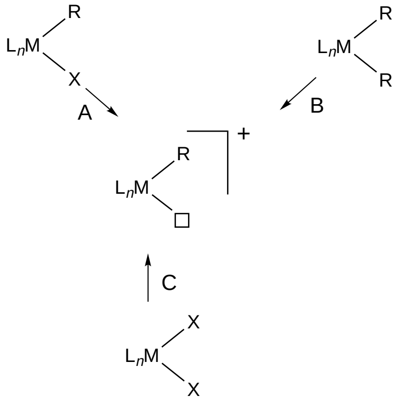
1.2. The Active Site

It is generally agreed that the catalytically active species in olefin polymerization is a coordinatively unsaturated cationic alkyl complex $[L_nMR]^+$ that is stabilized by several ligands L (Scheme 2). To generate such species several methods can be employed; three different routes (A, B, and C) are shown in Scheme 2.



Scheme 2. Three different routes to the catalytically active species $[L_nMR]^+$ (see text for details). □ represents the site of coordinative unsaturation.

Route A involves the abstraction of an anionic ligand (e.g. a halide) and its substitution for a "noncoordinating" anion by a salt elimination. Common reagents are $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[8] or silver salts such as $AgBF_4$ or $AgOSO_2CF_3$ (AgOTf) for the later transition metals. Route B involves the abstraction of an alkyl ligand or, more strictly, an alkyl anion. Reagents used for these ligands are, for example, $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$, $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[8] or $B(C_6F_5)_3$. Whereas the trityl reagent is an abstracting agent, the anilinium salt and the acid remove the alkyl ligand by protonation. In the case of $B(C_6F_5)_3$ the alkyl ligand is only partly abstracted leading to "cation-like" catalytic species.[9, 10] The applications of perfluorophenyl-substituted boranes and borates as cocatalysts have been recently reviewed.[11]

Route C is a combined alkylation and abstraction process, which can be achieved by treating a dihalide procatalyst first with an alkylating species and then with one of the aforementioned alkyl-abstracting agents, for example a trialkylaluminum compound followed by $B(C_6F_5)_3$. Some reagents can perform both processes, for example, alkylaluminum halides and especially alumoxanes such as methylalumінoxane (MAO). Albeit the structure of MAO is still largely unknown, the high activities and long catalyst lifetimes it affords are well documented and still the subject of ongoing study.[12–15]

Besides these classical activation methods, an alternative strategy for the generation of a catalytic active species has been introduced by Erker et al.[16] Treatment of a $[Cp_2Zr(\text{butadiene})]$ complex (**C**) with $B(C_6F_5)_3$ results in a metallocene-borate-betaine system (**D**), which is highly active in olefin polymerization (Scheme 3).[17, 18] In these systems the cationic and anionic parts are combined within the same molecules, "zwitterionic metallocenes".[19]


V. C. Gibson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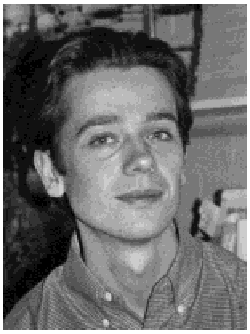
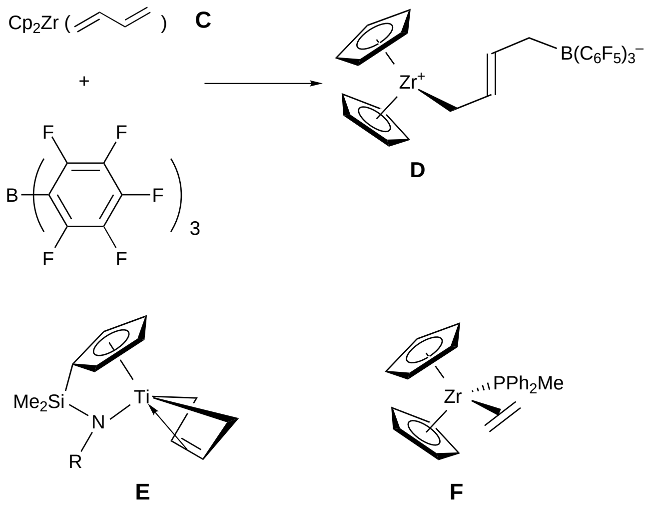

D. F. Wass

Vernon C. Gibson, born in 1958 in Grantham, England, studied chemistry at the University of Sheffield before moving to the University of Oxford, where he was awarded a D. Phil. in 1983 for work on the coordination and organometallic chemistry of the early transition metals carried out in the group of M. L. H. Green. He then spent two years as a NATO postdoctoral researcher at the California Institute of Technology with J. E. Bercaw before returning to England to take up a lectureship in chemistry at Durham University in 1986. He was appointed to a Chair of Chemistry at Durham sponsored by BP Chemicals in 1993. In 1995 he and his group moved to Imperial College, London, where he is Head of the Centre for Catalysis and Advanced Materials.

George J. P. Britovsek, born in 1966 in Heerlen, The Netherlands, studied chemistry at the Technische Universität Aachen (Germany). In 1993 he earned his doctorate from this university under the direction of W. Keim. He then spent two years as a postdoctoral researcher at the University of Tasmania (Australia) with K. J. Cavell, before joining the group of V. C. Gibson at Imperial College in London in 1996.

Duncan F. Wass was born in Leicester, England, in 1973. After studying chemistry at Durham University, he moved to Imperial College in 1995 where he is working for his Ph.D. under the supervision of V. C. Gibson.



Scheme 3. The zwitterionic approach to active polymerization catalysts.

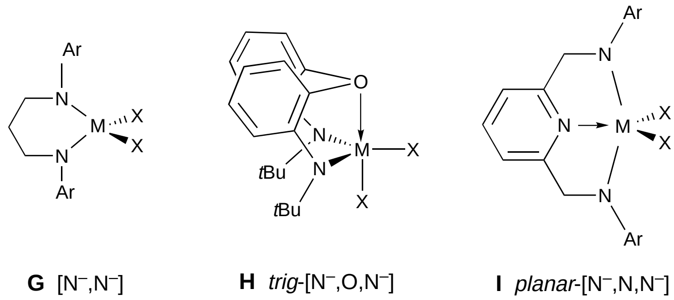
Similarly Devore and co-workers independently demonstrated the same principles for constrained-geometry titanium complexes **E**.[20] Piers and co-workers have shown recently that simple alkenes, for example coordinated ethylene in $[Cp_2Zr^{II}(C_2H_4)(PPh_2Me)]$ (**F**), also react with $B(C_6F_5)_3$ to form a zwitterionic metallocene capable of initiating olefin polymerization.[21]

In this review, except for those cases where well-defined catalysts are reported, we have not considered in any detail the method of activation employed. By far the most common approach has been activation of a dialkyl or dihalide precursor with MAO. In these cases the alkyl or halide group are referred to as a generic group X.

1.3. Ligands

The attendant ligands in polymerization-active metal complexes have four important roles: 1) control over the metal coordination number, 2) control over the metal coordination geometry, 3) control over the formal oxidation state of the metal, and 4) steric protection of the active site and influence over (stereo)selectivity. To assist the reader in categorizing polymerization-active metal–ligand combinations and thereby illuminate possible ways forward for future catalyst design, we have used a simple classification system that allows the ligands to be categorized according to the number and nature of the donor atoms and also the ligand charge, including an indication of which metal-attached ligand atoms bear the formal charge.

By way of example, consider the series of active zirconium procatalysts **G**–**I** (Scheme 4). The choice of chelating dianonic diamide ligands allows zirconium(IV) dichloro fragments to be stabilized either in a pseudo-tetrahedral environment for **G** or in distorted trigonal-bipyramidal environments for **H** and **I**. Moreover, the choice of an ether or pyridyl bridge influences the relative dispositions of the metal-attached atoms. In the case of **H** there is a trigonal arrangement of the N,O,N atoms of the ligand with the oxygen occupying the axial site of the trigonal bipyramid, while in the case of **I** the N,N,N tridentate chelating ligand binds in a planar arrangement, thereby leaving the chloro ligands to occupy the equatorial sites of the trigonal bipyramid. The ligands present in **G**, **H**, and **I** may be represented as $[N^-,N^-]$, *trig*-$[N^-,O,N^-]$, and *planar*-$[N^-,N,N^-]$, respectively. A description of this kind will be found adjacent to the pictorial representations of the procatalysts under discussion here, but will not be elaborated upon.



Scheme 4. Examples of zirconium(IV) procatalysts to illustrate the ligand classifications.

1.4. Catalyst Activities

The main focus of this review is catalyst performance for ethylene polymerization, though reference to other α-olefins is included wherever they have been reported. A "health warning" has to be applied when comparing catalyst activities reported by different groups of researchers, since experimentally determined values are highly dependent upon the precise reaction conditions, including stirring rate and the configuration of the reactor. Also, often little or no information is given about the kinetic profile or lifetime of the catalyst, with the consequence that a short polymerization run with a catalyst that is active only for 30 seconds before dying may give an "inflated" figure of merit compared to an activity reported for a one-hour run. Information about the catalyst's kinetic profile is very useful in allowing the most appropriate operating conditions to be chosen. For example, solution-phase catalysts generally require shorter reactor residence times than for a supported gas-phase catalyst.

To give the reader some feeling for how active a particular catalyst is compared to other systems, we have converted the activity figures available in the literature to units of $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ and placed the catalyst on a scale of merit ranging from very low to very high, as shown in Table 1.

Table 1. Rating of the effectiveness of a catalyst based on its activity.

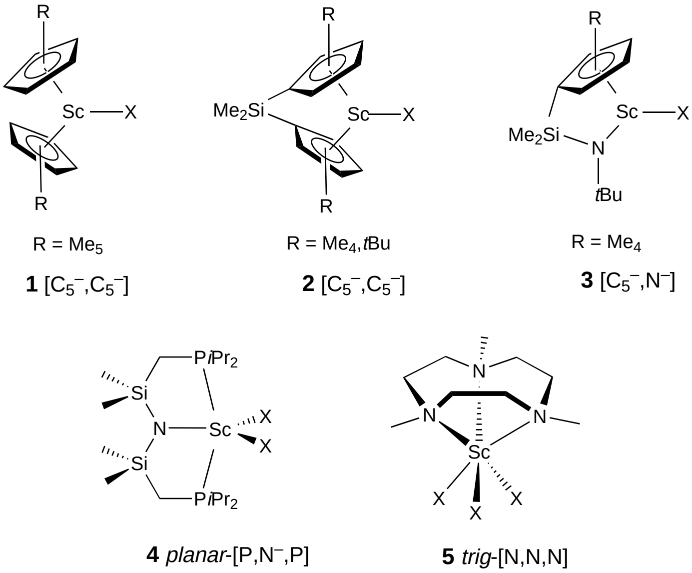
Rating	Activity $[g\,mmol^{-1}\,h^{-1}\,bar^{-1}]$
very low	< 1
low	1–10
moderate	10–100
high	100–1000
very high	> 1000

2. Catalysts with Group 3 and Rare Earth Metals

2.1. Group 3 Metal Catalysts

Neutral Group 3 alkyl complexes of scandium and yttrium are isoelectronic with Group 4 cationic alkyl complexes; compare, for example, $[Cp_2ScR]$ and $[Cp_2ZrR]^+$. This analogy has been used in the design of Group 3 olefin polymerization catalysts, as exemplified by the complexes shown in Schemes 5 and 6.

A potentially significant advantage of Group 3 catalysts is that they are single-component catalysts; no cocatalyst is needed. Commonly the neutral alkyl complexes, $[\{L_2MR\}_2]$, are dimeric in the solid state and in solution, and react with H_2 under mild conditions to yield the corresponding hydrides, $[\{L_2MH\}_2]$. Monomeric complexes have been obtained through the use of very bulky ligands or the addition of a donor ligand. The general low olefin polymerization activity of scandium complexes such as **1**–**3** (Scheme 5) has enabled detailed mechanistic investigations of the polymerization process.[22–26] Mono(pentamethylcyclopentadienyl)alkoxy scandium compounds have not shown any polymerization activity, probably due to the formation of an oxygen-bridged complex;[27] this is in contrast to observations made for analogous yttrium complexes (see below).[28] An anionic scandium complex with a dianionic dicarbollide ligand was found to be remarkably unreactive towards ethylene,[29] similar to the analogous neutral Group 4 titanium complex.[30] Most of the ligand systems used in Group 3 catalysts have followed from ligands that have been shown to be successful for Group 4 systems, although the Group 3 metals are generally much less well explored. Recently, scandium procatalysts containing tridentate ligands have been described, one containing a monoanionic *planar*-[P,N⁻,P] amide-diphosphane ligand (**4**), the other a neutral *trig*-[N,N,N] triazacyclononane ligand (**5**). Both are capable of polymerizing ethylene, though no activity figures were given.[31, 32]

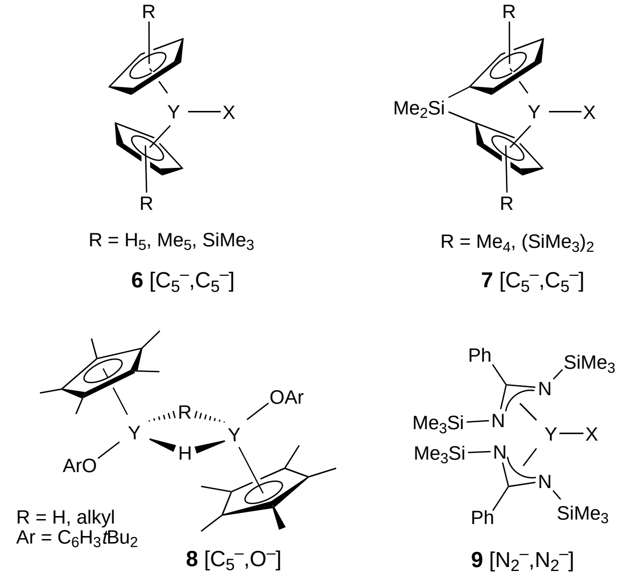


1 [C5⁻,C5⁻] **2** [C5⁻,C5⁻] **3** [C5⁻,N⁻]

4 *planar*-[P,N⁻,P] **5** *trig*-[N,N,N]

Scheme 5. Scandium complexes used as olefin polymerization catalysts.

Ligand design for organoyttrium olefin polymerization catalysts has also been following the trends of Group 4 catalysts (Scheme 6). Bis(cyclopentadienyl) complexes **6** have been the first reported to show moderate activity as ethylene polymerization catalysts (42 g mmol⁻¹ h⁻¹ bar⁻¹).[33] ansa-Metallocene analogues **7** have been investigated by the groups of both Bercaw and Yasuda, the latter has reported high activities for the polymerization of ethylene (584 g mmol⁻¹ h⁻¹ bar⁻¹).[34–37] The reaction of hydridoyttrium complexes bearing bulky aryloxide ligands with ethylene has been reported to lead to the rapid formation of polyethylene. No quantitative data has been given, but valuable mechanistic information has been obtained from the reaction of the bridged hydride initiator **8** with olefins.[28, 38, 39] Benzamidinate ligands (**9**) have been employed by Teuben and co-workers which have shown only very low ethylene polymerization activity.[40, 41]

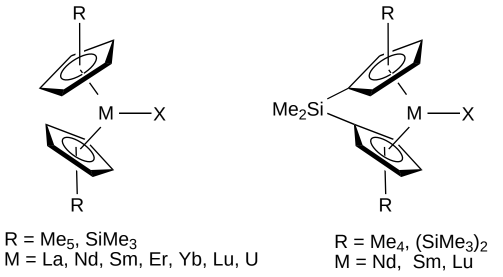


6 [C5⁻,C5⁻] **7** [C5⁻,C5⁻] **8** [C5⁻,O⁻] **9** [N2⁻,N2⁻]

Scheme 6. Yttrium complexes used as olefin polymerization catalysts.

2.2. Rare Earth Metal Catalysts

Lanthanide- and actinide-based olefin polymerization catalysts (**10**, Scheme 7) have invariably been stabilized with substituted cyclopentadienyl ligands. The first reports on the application of organometallic complexes of rare earth metals in ethylene polymerization appeared in 1978. Ballard and co-workers at ICI reported moderate catalytic activities at 100 °C (82 g mmol⁻¹ h⁻¹ bar⁻¹) using an alkyl metallocene complex of erbium,[33] and Marks et al. described bis(pentamethylcyclopentadienyl)uranium monochloride as a potent catalyst for ethylene polymerization.[42] Mechanistic studies of the reversible insertion of propene into the Lu–H bond of $[\{(C_5Me_5)_2LuH\}_2]$ with subsequent competitive β-H and β-Me elimination were reported a few years later by Watson and co-workers at DuPont. They have also shown that alkyl metallocene complexes of lutetium are ethylene



10 $[C_5^-,C_5^-]$ **11** $[C_5^-,C_5^-]$

Scheme 7. Lanthanide and actinide metallocenes investigated as olefin polymerization catalysts.

polymerization catalysts with moderate activity ($66\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$).[43–45] Studies by Schumann, Marks, and co-workers on hydride metallocene and ansa-metallocene complexes of lanthanum, neodymium, samarium, and lutetium (**11**) have shown remarkably high activities ($146\,400\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ for lanthanum). However, these figures are only initial activities, as polymerizations have been run only for a very short time (typically five seconds).[46–48] The corresponding alkyl metallocene complexes ($X = CH(SiMe_3)_2$) of La, Nd, and Lu are reported to be inactive towards ethylene at room temperature.[48] In contrast, alkyl metallocene complexes ($X = CH(SiMe_3)_2$) of samarium have shown moderate activities,[37, 49] and the Nd complex has been reported to be a "good" catalyst at higher temperatures (160 °C).[50]

3. Group 4 Metal Catalysts

In the search for new non-metallocene olefin polymerization catalysts, the vast majority of recent research effort has been directed towards the synthesis of alternative Group 4 catalysts. The wide variety of procatalysts that has been investigated necessitates a more systematic treatment of the differing ligand types. In Section 3.1 procatalysts of the type $[L_nMX_2]$ which, when activated, give rise to cationic alkyl active sites $[L_nMR]^+$ are described. This section is further divided according to carbon-, nitrogen-, and oxygen-based ligand types. Section 3.2 outlines applications of dianionic ligands ($(L^2)^{2-}$) to generate neutral 14-electron complexes $[L^1L^2MR]$ (where L^1 is typically a monoanionic Cp ligand) as the active centers.

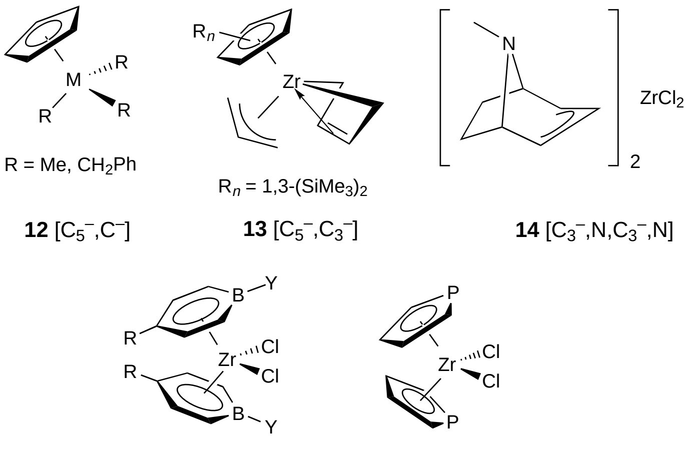
3.1. Cationic Group 4 Metal Complexes

3.1.1. Carbon-Based Ligands

3.1.1.1. Alkyl Ligands $[C^-]$

Simple homoleptic σ-hydrocarbyl complexes of Group 4 transition metals, for example $[Ti(CH_2C_6H_5)_4]$ or $[Zr(CH_2C_6H_5)_4]$, have produced active ethylene polymerization catalysts when activated with suitable Lewis acids such as MAO, $[Me_2NHPh][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, or $B(C_6F_5)_3$.[51–54] Only moderate activities are obtained with these systems.

For monocyclopentadienyl trialkyl complexes **12** (Scheme 8), where the catalyst $[Cp^*TiMe_2]^+$ ($Cp^* = C_5Me_5$) contains a ligand system that is a combination of a Cp ligand and an alkyl ligand $[C^-,C_5^-]$, moderate activities have been reported, both by Baird et al. ($46\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$)[55–57] and by Zambelli et al. ($80\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$).[52, 58] Ethylene polymerization results obtained by Bochmann et al. have shown that the order of activity is $[Cp_2ZrR]^+ > [CpZrR_2]^+ > [ZrR_3]^+$.[53] One Cp–aryl combination, where aryl = C_6F_5, has been reported by Baird and co-workers to give moderate activity for ethylene polymerization ($16\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$).[57]



12 $[C_5^-,C^-]$ **13** $[C_5^-,C_3^-]$ **14** $[C_3^-,N,C_3^-,N]$

15 $[C_5B^-,C_5B^-]$ **16** $[C_4P^-,C_4P^-]$

Scheme 8. Group 4 procatalysts with alkyl $[C^-]$, allyl $[C_3^-]$, and modified Cp $[C_nX^-]$ ligands.

3.1.1.2. Allyl Ligands $[C_3^-]$

Compared to alkyl ligands (two-electron donor) and a cyclopentadienyl ligand (six-electron donor) the intermediate allyl ligands (four-electron donor) have received little attention as spectator ligands in olefin polymerization catalysis. This may be due to the intrinsic higher reactivity of the allyl ligand compared to the cyclopentadienyl ligand. One report has described the use of a [Cp(allyl)Zr(dienyl)] complex (**13**, Scheme 8) which can be activated with $B(C_6F_5)_3$ (the method described by Erker et al.[16]) to a zwitterionic diallyl zirconium complex. Moderate polymerization activities are observed for this system ($98\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$), but the broad molecular weight distributions suggest the loss of active site uniformity.[59] Bergman and Lavoie have shown recently that allyl ligands with an additional donor $[C_3^-,N]$ are suitable ligand systems to generate zirconium complexes **14** with moderate ethylene polymerization activity ($17\,g\,mmol^{-1}\,h^{-1}\,bar^{-1}$).[60]

3.1.1.3. Cp Analogues $[C_5X^-]$ and $[C_4X^-]$

One modification of a Cp ligand is formally obtained by the insertion of a BY unit into the Cp ring, resulting in a boratabenzene $[C_5B^-]$ ligand. Zirconium complexes using boratabenzene ligands **15** (Scheme 8) have been reported by Bazan et al., and high polymerization activities are observed (105 g mmol^{-1} h^{-1} bar^{-1}) when it is used in combination with MAO.[61, 62] Interestingly, changing the Y substituent on boron from diisopropylamine to phenyl or ethoxide increases the rate of β-elimination, which results in the formation of lower molecular weight oligomers instead of polymer.[63] In combination with a constrained-geometry titanium catalyst, branched polyethylene has been produced.[64]

Another Cp analogue is obtained by the substitution of a CH unit for a P atom, resulting in phosphacyclopentadienyl ligands $[C_4P^-]$ (**16**, Scheme 8), which have been investigated by a number of research groups.[65–68] These catalysts generally afford very high activities, comparable to that of zirconocene dichloride.

3.1.2. Nitrogen-Based Ligands

3.1.2.1. Amide Ligands $[N^-]$

During the past ten years it has emerged that Group 4 metal complexes containing amide ligands are promising systems for applications in olefin polymerization catalysis. A formal lower electron count ($[(R_2N)_2ZrR]^+$ is a 10-electron species; compared with 14-electrons for $[Cp_2ZrR^+]$) is likely to result in a more electrophilic and therefore potentially more active catalyst fragment.

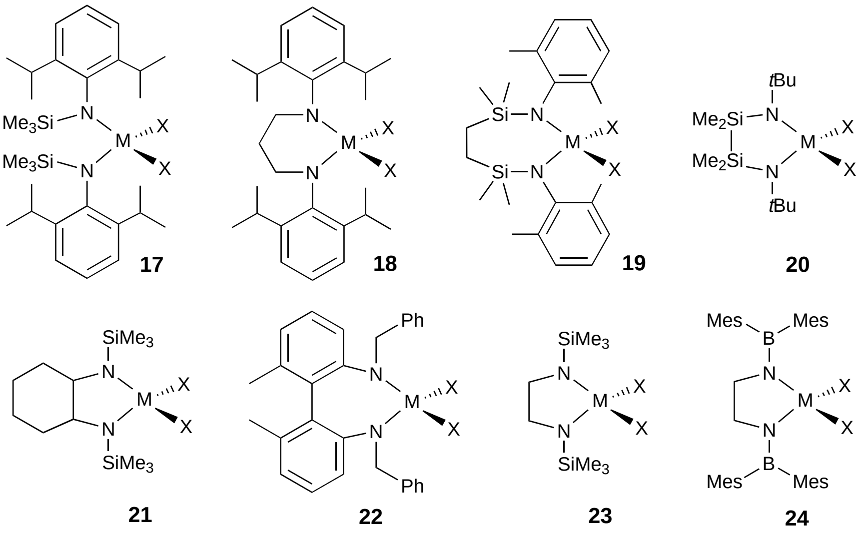
A few reports on the use of monodentate amide ligands have appeared, featuring either trimethylsilyl or bulky aryl substituents on nitrogen.[69, 70] Moderate activities (13 g mmol^{-1} h^{-1} bar^{-1}) are reported for zirconium complex **17** (Scheme 9) using MAO as a cocatalyst. In contrast, bis(amido) complexes containing a bidentate $[N^-,N^-]$ ligand system have received quite a lot of attention during the past two years. The different catalyst precursors are shown in Scheme 9.

Olefin polymerization activities obtained with these complexes vary significantly and decrease in the order from **18** to **24**. Activities are very low to low in the case of complexes **23**[73] and **24**.[71, 72] Moderate activity (13 g mmol^{-1} h^{-1} bar^{-1}) is observed with the biphenyl derivative **22** investigated by Cloke et al.[74] Zirconium compounds of type **21** have shown moderate activities (50 g mmol^{-1} h^{-1} bar^{-1});[75] no polymerization activity data has been given for the titanium analogue.[76] Complex **20**, containing a silicon backbone, was found to be considerably more active (100 g mmol^{-1} h^{-1} bar^{-1}) than its carbon backbone analogue **23**. A lowering of the electron density on the metal center and an overall stabilizing effect are believed to be the reasons for this "silicon effect".[77] For the diamide system **18**, developed by McConville and co-workers, no activity data on ethylene polymerization is disclosed, but α-olefin polymerization results indicate very high activity.[78–81] For the titanium complexes, living polymerization of 1-hexene has been reported.[79] The silicon-bridged diamide complexes **19** developed in our laboratory also form highly active ethylene polymerization catalysts (990 g mmol^{-1} h^{-1} bar^{-1}). Polymerization activity and kinetic profile are dramatically influenced by the chelate ring size.[82] Both systems contain bulky aryl substituents on the nitrogen donors which probably provide steric protection to avoid attack of the cocatalyst (MAO) on the amide ligand. Such an attack may cause catalyst deactivation either by complete loss of the ligand, as observed by Eisen and Mack,[83] or by intramolecular C–H activation; as observed by Horton and de With.[84] In both cases the resulting complexes still give an active catalytic system, but for reasons other than those intended.

3.1.2.2. Combinations of an Amide Ligand with Other Ligands

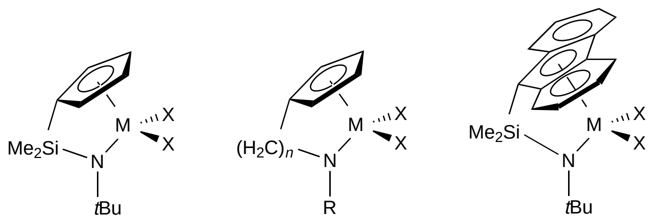
With Cp Ligands $[N^-,C_5^-]$

An important class of olefin polymerization catalysts has been developed at Dow and Exxon, by combining Cp ligands with an amide functionality $[N^-,C_5^-]$ to form a hybrid "half-metallocene", the "constrained-geometry catalysts" (CGC; **25**, Scheme 10).[70, 85, 86] These catalyst systems are highly active (1500 g mmol^{-1} h^{-1} bar^{-1}) and are under development for commercial exploitation. The titanium complex **25** (M = Ti, X = benzyl), when activated with MAO, gives good incorporation of 1-hexene comonomer.[86] More recently, variations on this theme have been reported in the academic literature. Teuben et al. and Green and co-workers have used a carbon linkage instead of silicon (**26**),[87–89] and Okuda et al. have investigated a series of different Cp analogues (**27**).[90] The copolymerization of ethylene and styrene has also been reported.[91] Like metallocenes, these constrained-geometry catalysts have been the subject of several theoretical studies.[92–95]



17 **18** **19** **20** **21** **22** **23** **24**

Scheme 9. Group 4 procatalysts containing diamide $[N^-,N^-]$ ligands. Mes = 2,4,6-trimethylphenyl.

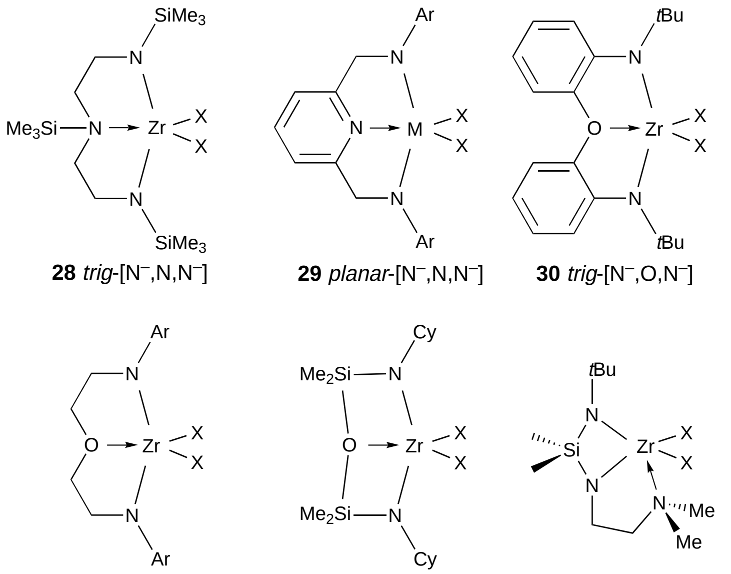


25 $[\mathrm{N}^-,\mathrm{C}_5^-]$ **26** $[\mathrm{N}^-,\mathrm{C}_5^-]$ **27** $[\mathrm{N}^-,\mathrm{C}_5^-]$

Scheme 10. Group 4 procatalysts with half-sandwich amide $[\mathrm{N}^-,\mathrm{C}_5^-]$ ligands.

With Additional Donors $[\mathrm{N}^-,\mathrm{Y},\mathrm{N}^-]$

Three different systems have been reported to date of a Group 4 bis(amido) complex with an additional donor Y—that is, an amine, pyridyl, or ether donor—incorporated in the ligand system. The ligand systems *trig*-$[\mathrm{N}^-,\mathrm{N},\mathrm{N}^-]$ (complex **28**, Scheme 11) developed by Horton et al.[96] and *planar*-$[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$ (complex **32**) developed by Bochmann and coworkers[75] have given moderate activities in the polymerization of ethylene (46 and 40 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$ respectively). The ethylene-bridged $[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$ system **31** has been shown to adopt both planar coordination (for X = Me) as well as the trigonal coordination mode (for X = benzyl); no details of ethylene polymerization have been given.[97] The analogous aryl-bridged ligand *trig*-$[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$ (**30**) has shown moderate activities (100 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$).[98] Interestingly, an additional pyridyl donor between the amide groups (**29**) affords very high activities (1500 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$);[99] in contrast, the titanium analogue has shown only very low activities for the polymerization of ethylene, possibly due to reduction to titanium(III).[100] Again bulky aryl substituents feature in this system, as in the $[\mathrm{N}^-,\mathrm{N}^-]$ bis(amido) complexes (Scheme 9). A recent example of a zirconium complex containing a $[\mathrm{N}^-,\mathrm{N}^-,\mathrm{N}]$ type ligand (**33**), synthesised by Schrock and coworkers, has been shown to be inactive in the polymerization of 1-hexene,[101] leading to the conclusion that the donor group should ideally be positioned between the amido functionalities.



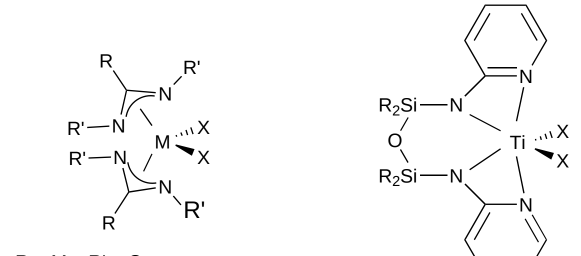
28 *trig*-$[\mathrm{N}^-,\mathrm{N},\mathrm{N}^-]$ **29** *planar*-$[\mathrm{N}^-,\mathrm{N},\mathrm{N}^-]$ **30** *trig*-$[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$

31 *trig*- or *planar*-$[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$ **32** *planar*-$[\mathrm{N}^-,\mathrm{O},\mathrm{N}^-]$ **33** $[\mathrm{N}^-,\mathrm{N}^-\mathrm{N}]$

Scheme 11. Group 4 complexes with diamide ligands that contain an additional donor (the ligand connectivity only is depicted). Cy = cyclohexyl.

3.1.2.3. Amidinate Ligands $[\mathrm{N}_2^-]$

An amidinate ligand, a monoanionic six-electron ligand, can formally be regarded as a combination of an amido and an imine donor. Only a few examples have been studied, either with a methyl substituent in the backbone and cyclohexyl groups at nitrogen[102] or with a phenyl or *p*-tolyl (p-$\mathrm{CH_3C_6H_4}$) group in the backbone and $\mathrm{SiMe_3}$ groups at nitrogen (**34**, Scheme 12).[103–106] Thus far only moderate activities have been obtained. Polymerization of styrene with these complexes has also been reported.[107] The imine moiety of the amidinate ligand can also be part of an aromatic system, for example a pyridine or pyrimidine ligand, giving aminopyridinato ligands (**35**). The complexes containing these ligands, however, have shown only low activity.[108]



R = Me, R' = Cy
R = $\mathrm{C_6H_5}$, p-$\mathrm{CH_3C_6H_4}$, R' = $\mathrm{SiMe_3}$

34 $[\mathrm{N}_2^-,\mathrm{N}_2^-]$ **35** $[\mathrm{NN}^-,\mathrm{NN}^-]$

Scheme 12. Group 4 bis(amidinate) procatalysts.

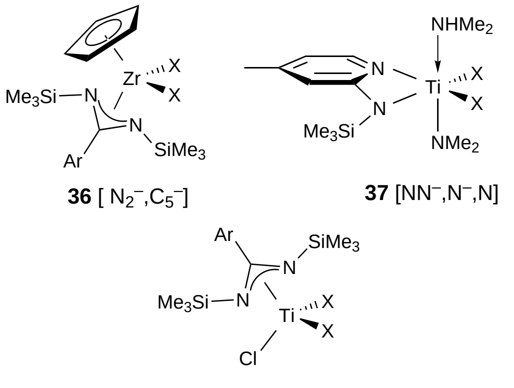
3.1.2.4. Combinations of an Amidinate Ligand with Other Ligands

With Cp Ligands $[\mathrm{N}_2^-,\mathrm{C}_5^-]$

Electronically related to the constrained-geometry catalysts—that is, a combination of a Cp and an amide ligand—combinations of Cp with amidinate ligands (**36**, Scheme 13) have been explored by Green, Teuben, and co-workers. Moderate activities have been obtained, using either the dihalide precursor in combination with MAO[109, 110] or the dimethyl precursor with $\mathrm{B(C_6F_5)_3}$.[111]

With Amide Ligands $[\mathrm{N}_2^-,\mathrm{N}^-]$

One report by Kempe et al. appeared in 1996 on the combined use of an amidinate-type ligand (aminopyridinate ligand) and an amide ligand in titanium and zirconium complexes (e.g. **37**, Scheme 13). No ethylene polymerization data has been reported, but polymerization results for propene and 1-butene show remarkably high activities.[112]



36 $[N_2^-,C_5^-]$ **37** $[NN^-,N^-,N]$

38 $[N_2^-,X^-]$

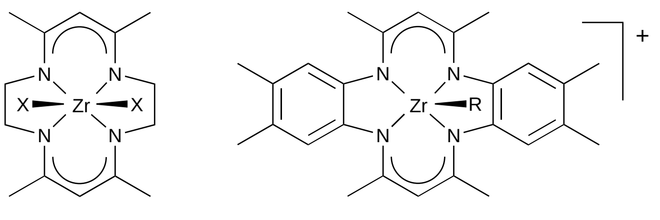
Scheme 13. Group 4 mono(amidinate) complexes with other ancillary ligands.

With Halide Ligands $[N_2^-,X^-]$

Monoamidinate trihalide complexes (**38**, Scheme 13) can be viewed as containing a combination of an amidinate ligand and a halide ligand, in analogy to monocyclopentadienyl trihalide complexes. Titanium complexes of this type have shown moderate activity (80 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$),[113] whereas the analogous zirconium complex are reported to give only very low activity as ethylene polymerization catalysts.[104]

3.1.2.5. *β-Diketimate Ligands $[N_2^-]$*

In 1993 Jordan and co-workers reported the synthesis of cationic d^0 Group 4 metal alkyl complexes incorporating tetraaza macrocyclic ligands and their application as olefin polymerization catalysts.[114] These *β*-diketimates can be regarded as higher homologues of amidinate ligands, as depicted in Scheme 14. The corresponding Zr complexes **39** are about 30 times less active than $[Cp_2ZrCl_2]$, thereby falling in the category of moderately active catalysts. Well-defined cationic complexes of type **40** have been reported recently, which exhibited only very low activity for the polymerization of ethylene.[115]



39 $[N_2^-,N_2^-]$ **40** $[N_2^-,N_2^-]$

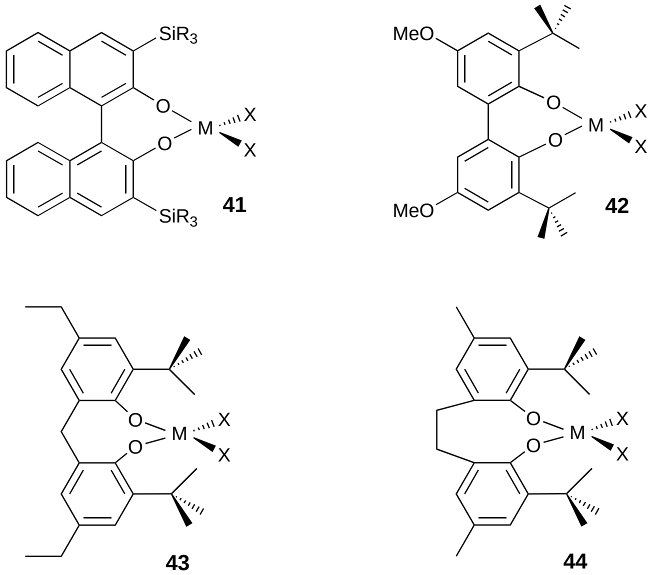
Scheme 14. Group 4 procatalysts with bis(diketimate) ligands.

Porphyrins have also been used as ancillary ligands to support zirconium– and hafnium–alkyl complexes.[116] However, these complexes proved unreactive towards ethylene.

3.1.3. *Oxygen-Based Ligands*

3.1.3.1. *Alkoxide Ligands $[O^-]$*

Terminal oxygen donors such as phenoxide ligands have been used successfully in olefin polymerization catalysis. In 1995 Schaverien et al. presented a study using various sterically hindered chelating phenoxide complexes of titanium and zirconium as olefin polymerization catalysts.[117] Ethylene polymerization tests with complexes **41** or **42** (Scheme 15) have shown only moderate activities, whereas complex **43**, with a methylene bridge, has given higher activity (130 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$). Okuda et al. have used ethylene-bridged bis(alkoxide) complexes **44** successfully in the copolymerization of ethylene with styrene, but no homopolymerization results have been reported.[118, 119] Theoretical calculations on these systems have been performed by Morokuma and co-workers.[120]



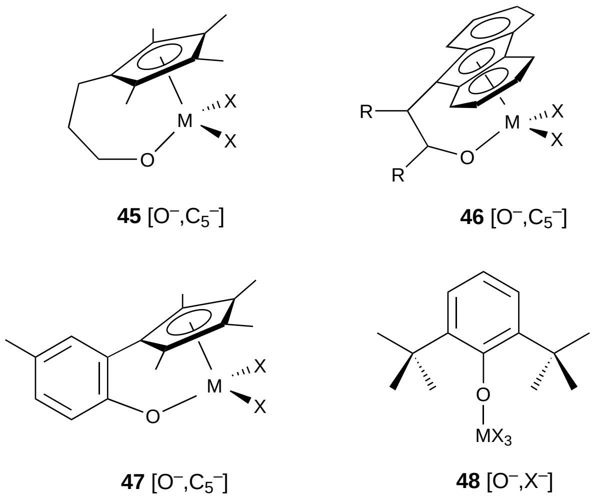
41 **42** **43** **44**

Scheme 15. Group 4 metal complexes bearing bidentate alkoxide $[O^-,O^-]$ ligands.

3.1.3.2. *Combinations of Alkoxides and Other Ligands*

With Cp Ligands $[O^-,C_5^-]$

Though various reports on the synthesis of Group 4 metal complexes using Cp–alkoxide ligands $[O^-,C_5^-]$ have appeared, only a few applications as olefin polymerization catalysts have been mentioned (Scheme 16). Hessen and co-workers have reported on the polymerization of propylene using well-defined Cp-alkoxide titanium complexes (**45**).[121] Rieger has shown that a fluorenyl alkoxide zirconium dichloride complex (**46**) can be activated with MAO to give an active olefin polymerization catalyst.[122] Marks et al. have shown that the combination of a Cp ligand and an aryloxide ligand (**47**) leads to a highly active polymerization catalyst for ethylene (2100 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$), propylene, and also styrene.[123] Furthermore, Baird et al. have reported on successful efforts utilizing monoalkoxide-Cp complexes as olefin polymerization catalysts, though no details have been given.[124]



45 $[\mathrm{O}^-,\mathrm{C}_5^-]$ **46** $[\mathrm{O}^-,\mathrm{C}_5^-]$ **47** $[\mathrm{O}^-,\mathrm{C}_5^-]$ **48** $[\mathrm{O}^-,\mathrm{X}^-]$

Scheme 16. Group 4 procatalysts with an alkoxide ligand and another ancillary ligand.

With Halide Ligands $[O^-,X^-]$

Another system worth mentioning in this context is a monoalkoxide titanium complex (**48**, Scheme16) as an olefin polymerization catalyst. This complex can be regarded as a combination of an alkoxide and a halide ligand, $[\mathrm{O}^-,\mathrm{X}^-]$. The catalytic activity of this complex was studied for the copolymerization of ethylene and styrene. However, a mixture of polyethylene and polystyrene and not a copolymer was obtained.[125]

3.1.3.3. Bis(alkoxides) with Additional Donors

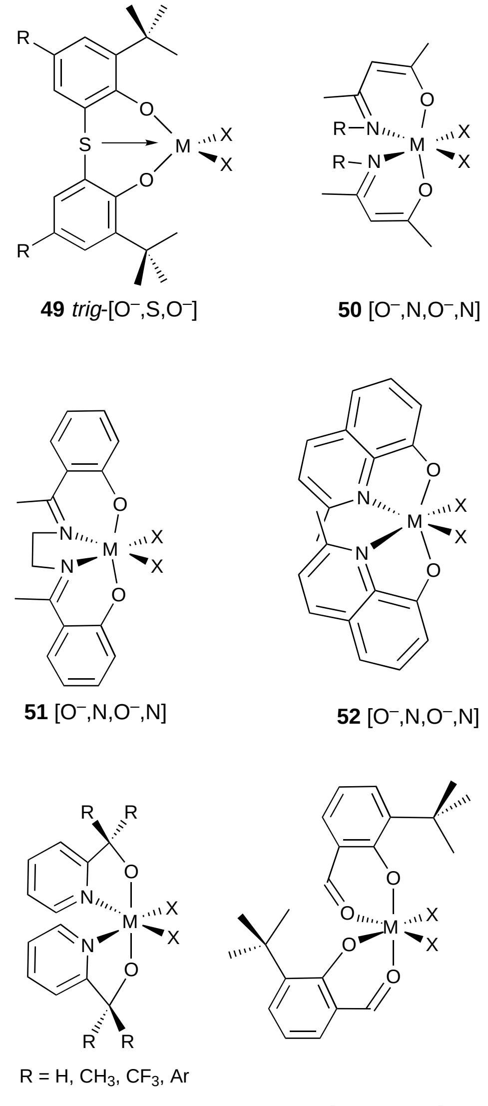
Monoanionic alkoxide ligands, being isonumeral[126] and isolobal with Cp^-, can bind to a metal using one σ and two π orbitals. They can potentially donate up to six electrons to the metal center, which would result in a cationic 14-electron species $[L_2MR]^+$. However, due to the higher electronegativity of oxygen, the alkoxide moiety is normally regarded as a four-electron ligand. This leaves the opportunity to add additional donors to generate a cationic 14-electron species.

Bis(alkoxides) with One Additional Donor $[O^-,Y,O^-]$

It has been shown in several reports that the activity of bis(alkoxide) Group 4 metal catalysts is dramatically improved by having an additional donor in the ligand backbone (Scheme 17). First reports appeared in 1989 by Kakugo et al. on a chelating phenoxide titanium complex (**49**).[127, 128] Further work by Schaverien et al.[117] and Okuda et al. have shown the importance of the additional intramolecular sulfur donor for high catalytic activity.[118, 129] Although the sulfur–titanium interaction is weak, it is likely to be of importance in stabilizing the active cationic species.[130]

Bis(alkoxides) with Two Additional Donors $[O^-,Y,O^-,Y]$

The application of N,O chelating ligands in Group 4 olefin polymerization catalysts has been studied by Jordan et al. Acen-type ligands (**50**, Scheme 17) were first investigated, but showed only moderate activity, probably due to the planar coordination geometry often observed for these ligands.[131, 132] Cavell et al. have shown that these compounds can also act as highly active oligomerization catalysts.[133] Salen-type complexes (**51**), which fall in this category, have given high activities (600 g mmol^{-1} h^{-1} bar^{-1}, supported on SiO_2).[134]



49 *trig*-$[\mathrm{O}^-,\mathrm{S},\mathrm{O}^-]$ **50** $[\mathrm{O}^-,\mathrm{N},\mathrm{O}^-,\mathrm{N}]$ **51** $[\mathrm{O}^-,\mathrm{N},\mathrm{O}^-,\mathrm{N}]$ **52** $[\mathrm{O}^-,\mathrm{N},\mathrm{O}^-,\mathrm{N}]$ **53** $[\mathrm{O}^-,\mathrm{N},\mathrm{O}^-,\mathrm{N}]$ **54** $[\mathrm{O}^-,\mathrm{O},\mathrm{O}^-,\mathrm{O}]$

R = H, CH_3, CF_3, Ar

Scheme 17. Group 4 procatalysts that contain alkoxide ligands with other donors.

Alkoxide ligands with a different nitrogen donor, for example pyridine (**52**, **53**), have been investigated by Jordan et al. In the case of **53**, for $R = CF_3$ moderate activities are reported (56 g mmol^{-1} h^{-1} bar^{-1}), whereas the complex with $R = CH_3$ shows no activity.[135, 136] It is noteworthy that for R = *p-tert*-butylphenyl the activity is significantly increased (280 g mmol^{-1} h^{-1} bar^{-1}).[137]

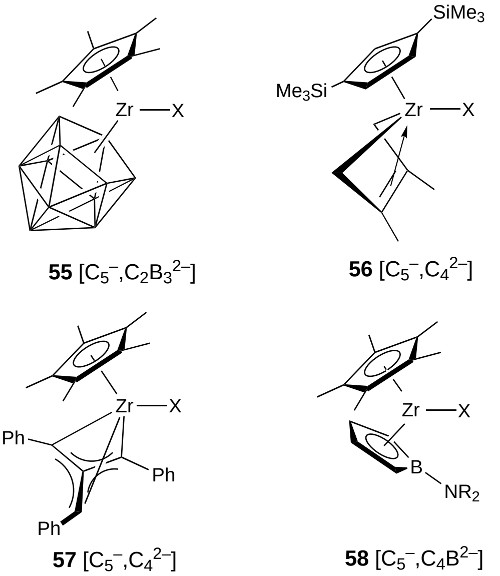
Finally, the use of additional oxygen donors (**54**) has been investigated by Matilainen and co-workers. In the presence of MAO, high catalytic activity is reported (400 g mmol^{-1} h^{-1} bar^{-1}), affording high molecular weight polyethylene with a broad molecular weight distribution.[138]

3.1.4. Halide Ligands [X⁻]

The use of simple halide ligands, as in $ZrCl_4$, together with a cocatalyst goes back to the early discoveries by Ziegler. Combinations of halides X^- with other ligands have been discussed above, except for the combination with Cp ligands, $[X^-,C_5^-]$. Monocyclopentadienyl titanium trichloride in combination with alkylaluminum cocatalysts is virtually inactive in olefin polymerization because of a fast reduction of the titanium center. Cyclopentadienyl ligands with pendant donors, for example amines, have shown increased stability and polymerization activity.[139] $[CpZrCl_3]$ gives moderate ethylene polymerization activities.[140]

3.2. Neutral Group 4 Metal Complexes

The formal replacement of a monoanionic Cp^- ligand in $[Cp_2MR]^+$ by isolobal, dianionic ligands reduces the overall charge by one unit, but leaves the gross structural and metal frontier orbital properties unchanged. Several dianionic ligands have been synthesized and converted into the corresponding monocyclopentadienyl zirconium complexes (Scheme 18). The complexes where X = Cl are commonly isolated as LiCl adducts, whereas the monoalkyl derivatives (X = alkyl) are stabilized by coordinated solvent.



55 $[C_5^-,C_2B_3^{2-}]$ **56** $[C_5^-,C_4^{2-}]$ **57** $[C_5^-,C_4^{2-}]$ **58** $[C_5^-,C_4B^{2-}]$

Scheme 18. Group 4 procatalysts containing one dianionic ligand.

Interestingly, these neutral catalysts offer an attractive alternative to metallocene catalysts as no cocatalyst should be needed. However, it has been proposed that the neutral charge on the active species may facilitate β-H elimination by weakening the M–C bond.[30] Moderate activity (70 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$) has been reported for the Cp–carborane zirconium complex **55**,[141] whereas the analogous titanium complex slowly dimerizes ethylene to butene.[30] The Cp–diene complex **56** reported by Bochmann and co-workers has given slightly higher activities (120 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$).[142] Analysis of the oligomers produced by a Cp–dienyl complex has shown that these catalysts behave as living polymerization catalysts.[143] Trimethylenemethane-based catalysts (**57**) described by Bazan and Rodriguez[144, 145] have shown high activities (400 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$). For the borrolide complex **58** no quantitative data on the polymerization have been reported.[146]

4. Group 5 Metal Catalysts

The most common approach to the design of Group 5 catalysts has been to exploit relationships between the monoanionic Cp ligand and isolobal dianionic fragments, similar to the approach outlined for neutral Group 4 catalysts in the previous section. Substitution of one Cp ligand from a Group 4 metallocene for an isolobal dianionic ligand and replacement of the metal by one from Group 5 gives access to high-valent 14-electron cationic alkyl species that may be expected to have metallocene-like reactivity. Complexes supported by a variety of such dianionic ligands have been investigated, although activities are generally disappointing compared to their Group 4 analogues.

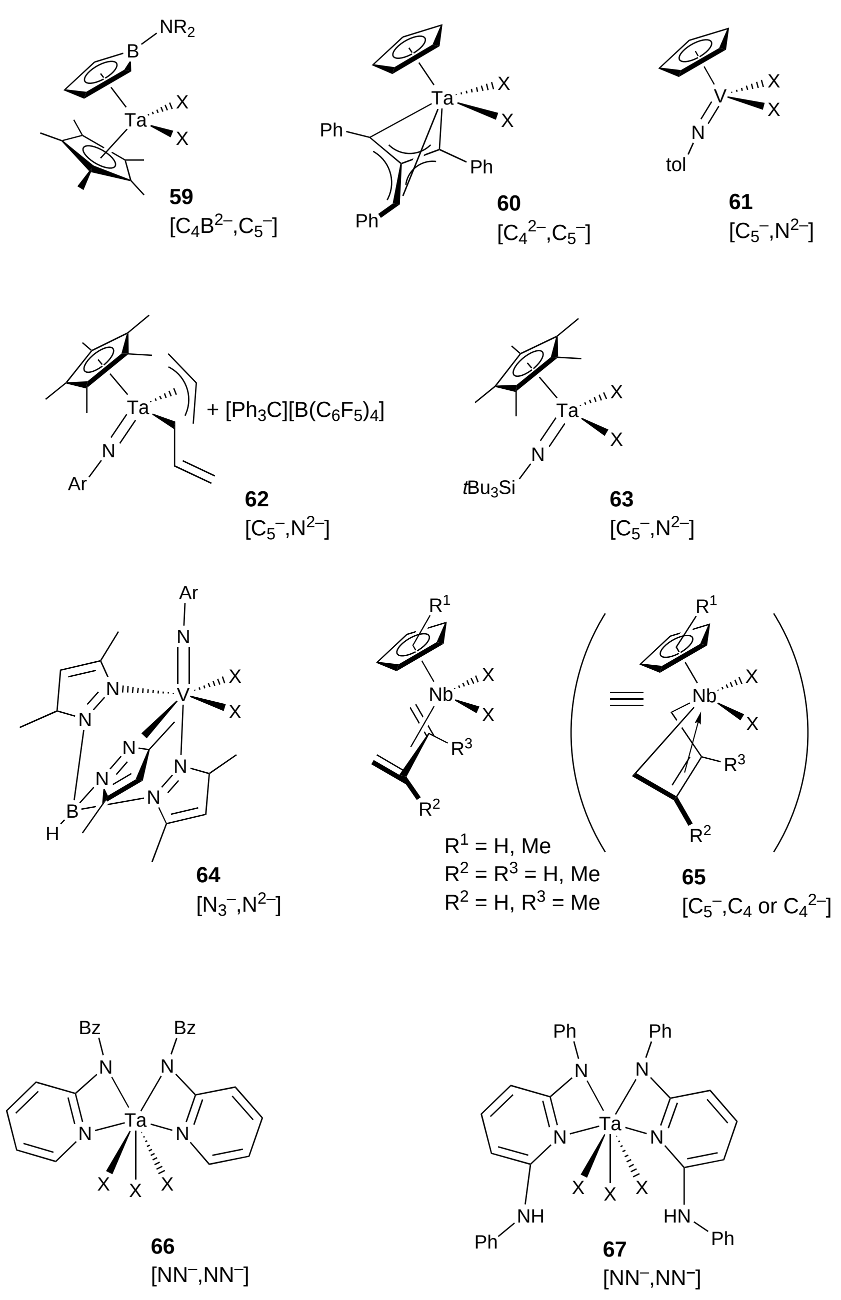
Substitution of a CH unit for a BNR_2 unit in a Cp ring gives the dianionic borollide ligand. Tantalum complex **59** (Scheme 19) is supported by this ligand and shows low ethylene polymerization activity.[147] It is believed the reactivity of this $[Cp^*Ta^V(\eta^5\text{-borollide})Cl_2]$ complex may be affected by a resonance contribution from $[Cp^*Ta^{III}(\eta^4\text{-diene})Cl_2]$. Complex **60** exploits the isolobal relationship between $[C(CH_2Ph)_3]^{2-}$ and Cp^- moieties.[145] Moderate polymerization activity of 40 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ is found.

An isolobal analogy between terminal imido and Cp groups can be drawn;[126] both groups donate electron density to a metal center through a σ and two π interactions (Scheme 20). The higher energy δ* orbitals of the Cp ligand can be neglected since they are not likely to make a significant contribution to the metal–Cp bonding at a d^0 metal center. A half-sandwich Group 5 Cp–imido fragment can therefore be considered isolobal with a Group 4 metallocene.

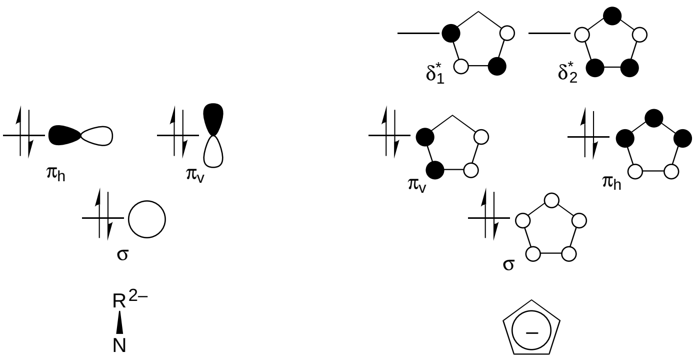
Half-sandwich vanadium compound **61** (Scheme 19) has a moderate activity (27 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$) when treated with MAO.[148] The analogous niobium system, although isolobal with zirconocene, is much less active.

Treatment of η^1,η^3-diallyl tantalum complex **62** with a trityl fluoroborate salt affords a catalytic system with low ethylene polymerization activity. The allyl substitution pattern is required for complex stability and, although the active catalyst may be considered a single-site allyl or alkyl cation, a high molecular weight material with broad polydispersity is formed.[149] The related compound **63** is supported by a very bulky silyl imido ligand and has moderate activity of 14 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ when treated with MAO. A material of similar molecular weight but narrower polydispersity is formed.[149]

Compound **64** not only exploits the isolobal relationship between Cp and the dianionic imido group but also that of Cp with the monoanionic trispyrazolylborate ligand. Moderate activity of 14 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ for ethylene polymerization is



Scheme 19. Group 5 metal procatalysts. tol = p-$CH_3C_6H_4$.



Scheme 20. Orbital diagram showing the isolobal relationship between cyclopentadienide and imide groups.

shown, and propylene is also polymerized to a low molecular weight material.[150]

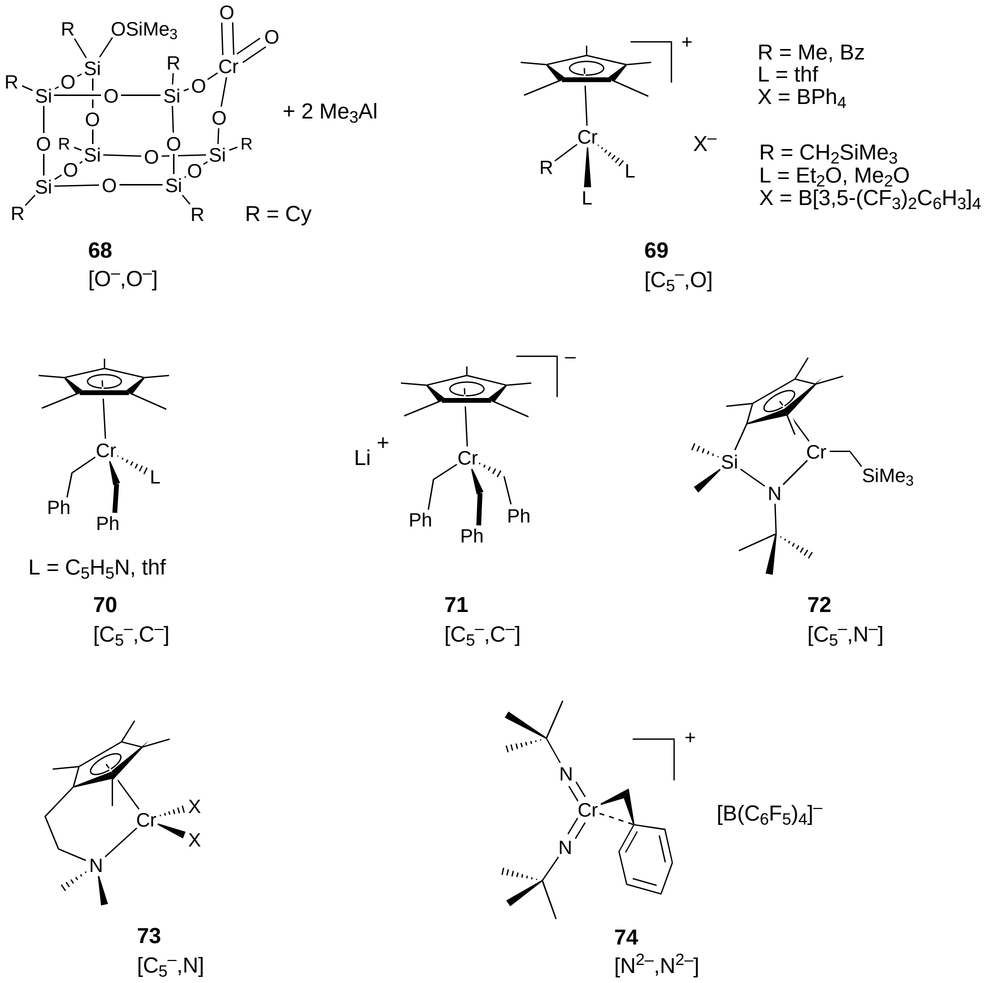
The niobium complexes **65** can be considered to contain either a neutral butadiene (C_4) ligand and a niobium(III) metal center or a dianionic butadienide (C_4^{2-}) ligand and a niobium(V) center. Polymerization activity is moderate at 39 g mmol^{-1} h^{-1} bar^{-1}, giving polyethylene with a molecular weight over 100000.[151–153] Polydispersities are very narrow when these catalysts are used, especially at reduced temperature where values as low as 1.05 have been obtained. These values are among the lowest for any polyethylene catalyst and suggest living polymerization may be occurring. Analogous tantalum catalysts have also been reported and show low activity.[152]

The most active Group 5 catalysts reported are compounds **66** and **67**.[154] These show very high activity, up to 4780 g mmol^{-1} h^{-1} bar^{-1} at 80 °C and 5 bar of ethylene pressure. At lower temperatures activity is considerably reduced. A range of polymer molecular weights are obtained depending upon the polymerization temperature, and polydispersities are narrow. MAO is used as a cocatalyst with the trihalide precursors, but no information regarding the nature of the active species is reported.

5. Group 6 Metal Catalysts

Group 6 heterogeneous catalysts play a central role in the commercial production of polyethylene. The Phillips catalyst, discovered as early as 1958 by Hogan and Banks,[155, 156] uses a silica support treated with CrO_3, subsequently reduced to a low-valent species that is the active catalyst. By contrast, the Union Carbide catalyst uses silica treated with divalent chromocene. Both systems are highly active and offer the advantage of not requiring any cocatalyst. The precise nature of the active sites of these systems is still to be elucidated. Perhaps for this reason—or the analytical problems associated with studying paramagnetic, low-valent chromium species—homogeneous analogues of these catalysts that parallel the discoveries in Group 4 metallocene/MAO systems have taken longer to be developed. Homogeneous chromium polymerization catalysts have been reviewed recently.[157, 158]

Many Group 6 catalysts are based on low-valent chromium species as models for heterogeneous catalysts. Perhaps the closest model is compound **68** (Scheme 21) reported by Feher et al.,[159, 160] which contains a chromyl fragment supported by two vicinal siloxy groups of a polyhedral oligosilsesquioxane.



68 $[O^-,O^-]$

69 $[C_5^-,O]$

70 $[C_5^-,C^-]$

71 $[C_5^-,C^-]$

72 $[C_5^-,N^-]$

73 $[C_5^-,N]$

74 $[N^{2-},N^{2-}]$

Scheme 21. Group 6 metal procatalysts.

Although this procatalyst contains chromium(VI) sites, an active catalyst is formed after treatment with Me_3Al, which is believed to reduce the metal center to chromium(III).

Theopold and co-workers have reported a number of catalysts based on chromium(III) supported by the pentamethylcyclopentadienyl ligand.[161–164] The most active system is the cationic compound **69**, which shows a moderate activity of 56 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ when noncoordinating anions are employed.[164] The active species is believed to be formed by dissociation of one labile tetrahydrofuran ligand, thus forming a $[C_5^-,O]$ donor set and enabling coordination of ethylene to the electrophilic metal center. Polyethylene materials are obtained with a range of molecular weights depending on the catalyst and conditions used, and the oligomerization of higher α-olefins is also reported. Theoretical calculations using $[Cr(H_2O)ClMe]^+$ as a model catalyst for these systems have been performed.[165]

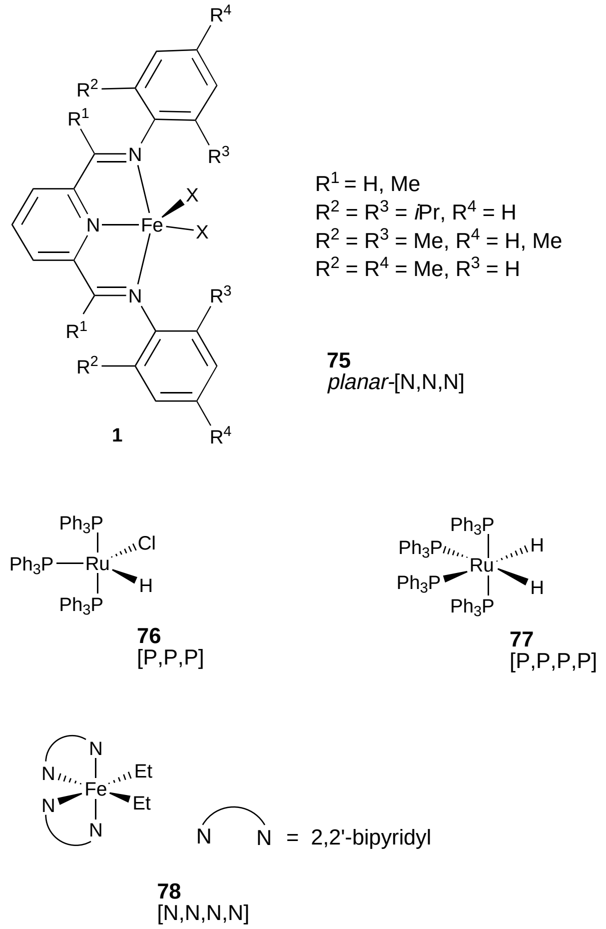
The neutral complexes **70** show low activity.[161] Again the active catalyst is formed by the loss of the labile ligand L. The related anionic compound **71** shows low activity,[161] but the active species in this case is believed to be identical to that of the neutral complex **70** and is formed by the loss of LiBz. This is supported by the inhibiting effect of added LiBz. Compound **72** is based on a Cp–amido constrained-geometry catalyst.[166] The activity reported is very low, and higher α-olefins are only oligomerized or isomerized. Attempted copolymerization of ethylene with higher α-olefins, in contrast to the use of Group 4 constrained-geometry catalysts,[70, 85, 86] results in no comonomer incorporation.

A very active catalyst is formed by treatment of **73** with as few as 100 equivalents of MAO.[167, 168] Activities as high as 8300 $g\,mmol^{-1}\,h^{-1}\cdot bar^{-1}$ are reported. These complexes are related to constrained-geometry systems, being based on linked Cp–amine $[C_5^-,N]$ ligands, and have been studied as models for the trimerization of ethylene to 1-hexene. Propylene is also polymerized, and ethylene and norbornene are copolymerized to an alternating copolymer.

An alternative approach to the development of Group 6 catalysts has been to extend the principles of isolobality exploited for the Group 5 metals. Replacement of both Cp groups of a Group 4 metallocene with isolobal, dianionic imido ligands enables high-valent chromium(VI) compounds with metallocene-like characteristics to be accessed. This extended isolobal relationship has been exploited in our group to develop the well-defined catalyst **74**.[169] Moderate ethylene polymerization activity of up to 65 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ is found.

6. Group 8 Metal Catalysts

One of the most recent additions to the small but growing number of highly active non-metallocene polymerization catalysts are the iron(II) complexes shown in Scheme 22.[170, 171] Complex **75** is based on a five-coordinate iron center supported by a neutral tridentate 2,6-bis(imino)pyridine ligand and, when activated with MAO, shows exceptionally high activity. Activity figures in many cases are comparable or even higher than those found for Group 4 metallocenes under analogous conditions. The molecular weight of the polyethylene material generated shows a marked dependency upon the aryl substitution pattern. Aryl substituents with only one small *ortho* substituent give highly active oligomerization catalysts with exceptionally high selectivities for the production of α-olefins.[170,172] Increasing the size of this substituent to



Scheme 22. Group 8 metal procatalysts.

a *t*Bu group, or placing substituents in both of the *ortho* positions, results in the formation of high molecular weight polyethylene. ^{13}C NMR analysis of these polymers reveals saturated end groups in addition to low levels of vinyl unsaturation. This is consistent with a termination mechanism involving alkyl group transfer to the aluminum cocatalyst in addition to β-H transfer. Thus, by judicious choice of ligand substituents and polymerization conditions, a range of materials from α-olefins to polyethylenes can be obtained.

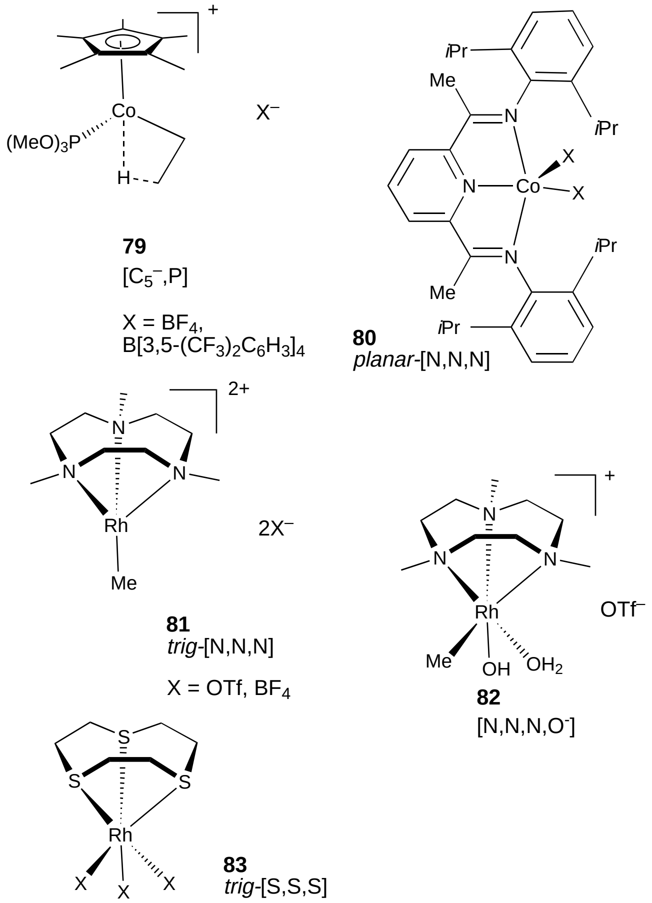
Only one other Group 8 ethylene polymerization catalyst has been reported to date.[173] The ruthenium complex **76** shows very low activity for the polymerization of ethylene. The kinetics of polymerization using this catalyst have been extensively studied. A branched polyethylene is reported to be produced.

A series of papers by Yamamoto and co-workers report the polymerization of functionalized vinyl monomers by iron and ruthenium complexes.[174–176] For example, complex **77**, although related to complex **76**, does not show any ethylene polymerization activity. Acrylonitrile, however, is polymerized with 57% conversion in five minutes.[176]

Complex **78** is reported to polymerize a range of monomers including methyl methacrylate, acrolein, methyl vinyl ketone, and acrylonitrile.[174] Conversion rates are low and ethylene is not polymerized. The mechanism for polymerization is proposed to be by a coordinative pathway involving the partial dissociation of one 2,2′-bipyridyl ligand.[175]

7. Group 9 Metal Catalysts

The most extensively studied example of the Group 9 catalysts is the cobalt(III) complex **79** (Scheme 23).[8, 177–181] This cationic compound shows a β-agostic interaction and inserts ethylene in a living fashion to form high molecular weight polymers with narrow polydispersity. Activities are low, the most active catalyst being obtained when noncoordinating counterions are employed. Higher α-olefins are only oligomerized, but end-functionalized polyethylene materials have been successfully synthesised with this system.



Scheme 23. Group 9 metal procatalysts.

The cobalt(II) complex **80** shows an activity of 460 g mmol^{-1} h^{-1} bar^{-1} when treated with MAO.[170, 171] Although this figure of merit represents the highest activity reported for a Group 9 system, it is an order of magnitude lower than for the analogous iron catalyst **75** (Scheme 22). The polyethylene obtained is end-capped with a vinyl group, an observation consistent with β-H elimination being the predominant chain-termination process.

The dicationic rhodium(III) complex **81**, containing the hard triamine donor triazacyclononane, is reported to be an active ethylene polymerization catalyst[182] although no activity figure is given. The supporting ligand in this case is considered a *trig*-[N,N,N] donor, in contrast to the *planar*-[N,N,N] ligands of the highly active catalysts **75** and **80**. This system is the first example of a catalyst capable of polymerizing ethylene in water.[183] The active species in aqueous solution is believed to be formed by the dissociation of the bound water molecule from **82**. Activity is extremely low, corresponding to only one turnover per day at 60 bar. Catalysis is also found to be sensitive to the pH value because of the equilibrium of species present in aqueous solution.

Related *trig*-[S,S,S] trithiacyclononane derivatives have recently been synthesized. The neutral procatalyst **83** has shown low activity for ethylene polymerization with MAO as cocatalyst.[184]

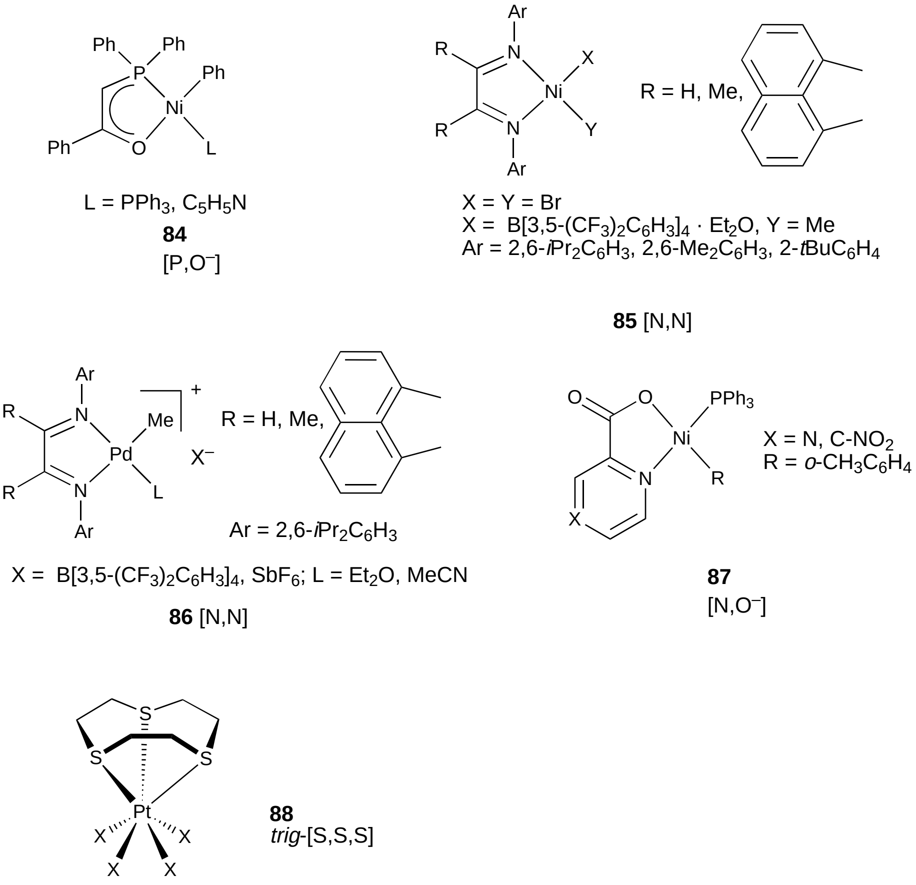
8. Group 10 Metal Catalysts

Group 10 compounds with anionic P,O ligands are well known to oligomerize ethylene, playing a central role in the Shell Higher Olefin Process (SHOP). There have also been reports that SHOP-type oligomerization catalysts can polymerize ethylene under certain conditions.[185–192] Compound **84** (Scheme 24), for example where L = PPh_3, shows very high polymerization activity, giving materials with molecular weights over 100000.[186, 187] Crucial to the formation of high molecular weight polymers rather than oligomers is the removal of L with phosphane scavengers such as $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene), or the use of more labile groups for L, such as pyridine or ylides. These catalysts have also been shown to be active for the copolymerization of ethylene with higher α-olefins or ω-functionalized α-olefins.[186] An alternative approach has been to support such catalysts on organic polymers.[185] Polyethylene is produced by these heterogeneous systems with very high activity.

Complex **87**, based on mixed N,O donor chelates, shows low polymerization activity.[193] Interestingly, the use of electron-withdrawing substituents or pyrazine donors is essential for polymerization to occur. Incorporation of simple pyridine donors result only in oligomerization.

The nickel(II) and palladium(II) systems reported by Brookhart and co-workers,[194, 195] based on square-planar cationic alkyl compounds supported by bulky diimine [N,N] ligands, were the first examples of late transition metal catalysts capable of polymerizing higher α-olefins as well as ethylene to high molecular weight polymers.

When treated with MAO, the nickel dibromide derivative of compound **85** shows very high activity, up to 11000 g mmol^{-1} h^{-1} bar^{-1}.[195] The well-defined cationic alkyl species is also active. β-Elimination from the growing polymer chain leads to chain branching or chain transfer. The formation of high molecular weight polymers is possible because the steric protection of the vacant axial coordination sites reduces the rate of associative displacement from β-eliminated olefin–hydride complexes and thus reduces chain transfer rates. A range of polyethylene materials with molecular weights up to 1×10^6 and degrees of branching from linear to over 70 branches per 1000 carbon atoms is accessible by simple variation of temperature, pressure, and ligand architecture. At low temperature, the polymerization is living, and di- and triblock ethylene/α-olefin copolymers can be synthesized.[196] Also at low temperature, propylene is polymerized to syndiotactic polyproylene by chain-end control.[197] At higher temperatures, α-olefins are polymerized to give more linear materials than expected because of β-elimination and reinsertion mechanisms leading to chain straightening.



Scheme 24. Group 10 metal procatalysts.

The analogous palladium(II) compounds **86** (Scheme 24) show more moderate activity to produce very highly branched amorphous polyethylene, with a range of molecular weights and up to 100 branches per 1000 carbon atoms. The mechanism of polymerization with these catalysts has been studied and the alkyl–olefin catalyst resting states characterized by NMR techniques. These catalysts are able to copolymerize α-olefins with functionalized comonomers such as methyl acrylate, resulting in highly branched random copolymers with ester groups on some chain ends.[198, 199] The mechanism for copolymerization is by 2,1-insertion of acrylate and chelate ring expansion, followed by insertion of ethylene units. Activities, however, are found to be much lower than for homopolymerization.

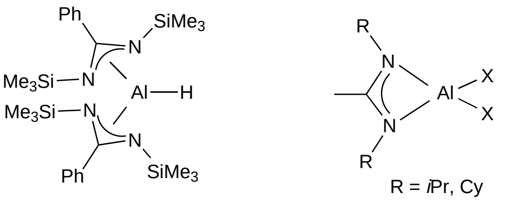
Calculations have been performed on both nickel and palladium systems.[200–203] These studies corroborate the crucial role of axial steric protection in the formation of high molecular weight polymers.[200] The development of these catalysts, both in terms of ligand modification and new activation pathways, continues apace.[204, 205]

One example of a platinum(IV) catalyst has been reported.[184] Trithiacyclononane-supported complex **88** shows a moderate activity of 12 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$ for the polymerization of ethylene with MAO activation. As with the related rhodium species **83**, no information as to the nature of the active catalytic species is reported.

9. Group 13 Metal Catalysts

Almost 40 years ago Ziegler et al. reported on "reactions of the aluminum–carbon bond with olefins". The "aufbau" reaction— that is, the stepwise addition of the Al–C bond of a trialkylaluminum compound to ethylene—yielded α-olefins under high pressure and temperature.[206] Activities of these trialkylaluminum compounds to form solid polyethylene have been extremely low.[207]

More recently, two reports have appeared in the literature describing homogeneous aluminum compounds that are able to polymerize ethylene under mild conditions. One system, reported by Teuben and co-workers,[208] features an aluminum hydride complex **89** (Scheme 25) containing two benzamidinate ligands. With ethylene, under moderate conditions (4 atm, 40 °C, 2 h), a small amount of polyethylene was obtained. No quantitative data have been reported.



89 $[N_2^-, N_2^-]$ **90** $[N_2^-]$

Scheme 25. Aluminum complexes used as olefin polymerization catalysts.

Another aluminum catalyst was reported recently by Coles and Jordan.[209] The neutral dialkylaluminum complex **90**, supported by only one benzamidinate ligand, is activated in an analogous fashion to many transition metal systems, by conversion into a cationic monoalkyl species. For example, activation of complex **90** with $[Ph_3C][B(C_6F_5)_4]$ in toluene has given an activity of 3 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$ under moderate conditions (2 atm, 85 °C). Although polymerization activites obtained thus far are low, these catalysts are significant as they represent the first examples of well-defined main group complexes acting as ethylene polymerization catalysts.

10. Summary

To help the reader to categorize the large array of olefin polymerization catalysts presented in this review, a summary of all catalysts discussed is given in Table 2. The catalysts are collected together according to the group in the periodic table within the activity ranges outlined in Table 1. Table 2 should be used as an indicator of activity trends, rather than an absolute measure of catalyst performance, since the activities are subject to polymerization conditions that may not have been optimized.

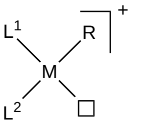
Table 2. Overview of catalysts discussed in this review and their ranking according to their activity.

Group	Activity[a]				
	very low <1	low 1–10	moderate 10–100	high 100–1000	very high >1000
3	Y: **9**	Sc: **1–3**	Y: **6** RE:[b] **10**	Y: **7**	RE:[b] **11**
4	Ti: **24**	Ti: **23**, **35**	Ti: **12**, **34**, **38**, **41**, **42**	Ti: **20**, **43**, **49**, **54**	Ti: **18**, **25**, **37**, **47**
	Zr: **24**, **38**, **40**		Zr: **13**, **14**, **17**, **21**, **22**, **28**, **30**, **32**, **34**, **36**, **39**, **41**, **42**, **50**	Zr: **15**, **53**, **55**, **56**, **57**	Zr: **16**, **18**, **19**, **25**, **29**
5		Ta: **59**, **62**	V: **61**, **64** Nb: **65** Ta: **60 63**		Ta: **66**, **67**
6	Cr: **72**	Cr: **70**	Cr: **69**, **74**		Cr: **73**
8	Ru: **76**				Fe: **75**
9	Rh: **82**	Co: **79** Rh: **83**		Co**:** **80**	
10		Ni: **87**	Pd: **86** Pt: **88**		Ni: **84**, **85**
13	Al: **89**	Al: **90**			

[a] Values given in units of $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$; [b] RE = rare earth metals.

Having reviewed some of the key developments in the search for new olefin polymerization catalysts, it is appropriate to examine more closely the factors that are important for the generation of high-activity catalysts. Three features are essential: 1) electron deficiency—all known catalysts are electron-deficient species. With the exceptions of a few 15- and 16-electron species, they mostly contain 14 or fewer electrons. 2) The active center must have a vacant coordination site adjacent to the growing polymer chain. 3) The active catalyst should preferentially bear a positively charged metal center which enhances the electrophilicity of the active site and also helps to inhibit certain deactivation pathways such as dimerization, for example as seen in certain neutral catalysts such as $[\{Cp_2ScH\}_2]$. It has also become increasingly clear, especially since the development of highly active late transition metal catalysts, that a fourth feature, steric protection, plays a crucial part in the stabilization of the active site once formed, its selectivity towards olefin substrates, and control over the molecular weight parameters of the resultant polymers.

These guiding features can be used to construct a chart of metal–ligand combinations that afford polymerization active metal centers. Active cationic catalysts may be represented by the general formula shown in Scheme 26, where L^1 and L^2 represent coordinated ligands, and R may be either a simple alkyl group in an initiating species or the extended alkyl chain of the growing polymer.



Scheme 26. Generic structure of a cationic olefin polymerization catalyst (see text for details). □ represents the site of coordinative unsaturation.

For the purpose of this exercise, the electron-counting formalism with charged ligands is employed, and the ligands are considered to donate their maximum available number of electrons; for example, the cyclopentadienyl group is a monoanionic Cp^- unit donating six electrons to the metal center (6e, −1), an imido moiety is a dianionic RN^{2-} unit contributing a maxiumum of six electrons in its linear bonding mode (6e, −2). The growing polymer chain is a monoanionic R^- unit contributing two electrons. The charged formalism lends itself readily to assignment of the oxidation state of the metal center and allows a matrix for cationic 14-electron complexes to be constructed according to metal oxidation state (Table 3).

It can be seen from Table 3 that, in addition to well-established active catalyst families such as the metallocenes and nickel- and chromium-based systems, the matrix allows other metal–ligand combinations to be identified that afford 14-electron cationic alkyl species, thereby highlighting potential new catalyst targets. Examples of some of the most active catalyst systems discovered to date in this class are shown in boldface.

One example of a recently discovered 14-electron cationic alkyl catalyst system highlighted in Table 3 is the [{bis(imino)pyridine}$FeCl_2$] system **75** (Scheme 22).[170, 171] Iron(II) requires a neutral two-electron donor ligand and a neutral four-electron donor ligand (corresponding overall to three two-electron donor ligands). The tridentate pyridyldiimine ligand is found to meet these requirements perfectly, and activation of the complex with MAO affords a highly active ethylene polymerization catalyst.

Finally, it should be recognized that not all olefin polymerization catalysts are 14-electron species, and not all are cationic either. In general, active catalysts have to be coordinatively unsaturated—that is, 16 electrons or less—and they may be cationic or neutral. For example, cationic 13-electron chromium(III),[157] dicationic 14-electron rhodium(III),[182] and neutral 15-electron chromium(III)[166] systems are known. Related charts can be drawn up for species with different electron counts, both neutral and charged, and these too may serve to help identify new catalyst families.

Table 3. A matrix of metal–ligand combinations that give cationic 14-electron complexes.[a]

	2, 0	2, −1	4, 0	4, −1	4, −2	6, 0	6, −1	6, −2
2, 0	$\mathbf{Ni}^{\mathbf{II}}$, $\mathbf{Pd}^{\mathbf{II}}$	Au^{III}	$\mathbf{Fe}^{\mathbf{II}}$, Ru^{II}	Co^{III}, Rh^{III}	Pd^{IV}, Pt^{IV}	Cr^{II}, Mo^{II}	Mn^{III}, Re^{III}	Fe^{IV}, Ru^{IV}
2, −1			Co^{III}, Rh^{III}	Pd^{IV}, Pt^{IV}		Mn^{III}, Re^{III}	Fe^{IV}, Ru^{IV}	
4, 0			Cr^{II}, Mo^{II}	Mn^{III}, Re^{III}	Fe^{II}, Ru^{IV}	Ti^{II}, Zr^{II}	V^{III}, Nb^{III}	Cr^{IV}, Mo^{IV}
4, −1				Fe^{IV}, Ru^{IV}		V^{III}, Nb^{III}	Cr^{IV}, Mo^{IV}	Mn^{V}, Re^{V}
4, −2						Cr^{IV}, Mo^{IV}	Mn^{V}, Re^{V}	
6, 0						Mg^{II}, Ca^{II}	Sc^{III}, Y^{III}	Ti^{IV}, Zr^{IV}
6, −1							$\mathbf{Ti}^{\mathbf{IV}}$, $\mathbf{Zr}^{\mathbf{IV}}$	$\mathbf{V}^{\mathbf{V}}$, $\mathbf{Nb}^{\mathbf{V}}$, $\mathbf{Ta}^{\mathbf{V}}$
6, −2								$\mathbf{Cr}^{\mathbf{VI}}$, Mo^{VI}

[a] The coordinated ligands L^1 and L^2 (Scheme 26) are represented by the designation (x, y), where x is the maximum available number of electrons and y is the charge.

11. Outlook

The field of α-olefin polymerization catalysis has developed dramatically over the past five years or so, with some of the most significant recent advances occuring for late transition metal systems. The discovery of a highly active family of catalysts based on iron, a metal that had no previous track record in this field, has highlighted the possibilities for further new catalyst discoveries. No longer need the search for new catalysts be restricted to metals that have a history of giving polymerization-active centers. The speed of catalyst discovery is likely to be limited only by the flair and imagination of the synthetic organometallic and coordination chemist for ligand design. The late transition metals especially are likely to provide fertile ground for future development, and the greater functional group tolerance of the late transition metals also offers the attractive prospect of polar comonomer incorporation. A relatively small amount of functionality can dramatically transform the adhesion and wetability properties of polyolefins; more heavily functionalized products offer the prospect of materials with totally new properties and performance parameters. It is clear that, for olefin polymerization catalysis, the process of catalyst discovery and development is far from over.

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