

INVITED REVIEW

Non-bridged half-metallocene complexes of group 4–6 metals with chelating ligands as well-defined catalysts for α -olefin polymerization

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Tremendous effort has been directed toward the design of an organic ligand framework around the catalytically active metal center of homogeneous catalyst precursors. This work is aimed at controlling not only the reactivity of the metal catalysts for α -olefin polymerization but also the molecular weight, molecular weight distribution, polymer microstructure and monomer content of the copolymers. Among the catalyst precursor categories, non-bridged half-metallocene complexes supported by a variety of chelating ligands are attractive catalyst motifs for ethylene homopolymerization, ethylene/ α -olefin copolymerization and stereoselective polymerization of α -olefins. These motifs are attractive in terms of their rather simple synthetic protocols and the wide range of potential architectural designs of the attached ligands. This review article summarizes recent developments regarding non-bridged half-metallocene complexes of group 4–6 metals with anionic chelating ligands. In contrast to the conventional metallocene initiators Cp_2MX_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), half-metallocene complexes of the type $\text{CpM}(\text{L}^\wedge\text{L})\text{X}_2$ (L^\wedgeL = chelating ligands) offer the advantage of catalyst modification. Steric and/or electronic modification of the coordination environment can be achieved by changing one cyclopentadienyl ligand of a metallocene complex to another ligand, such as three-, four-, five-, six- or seven-membered chelates having bidentate or tridentate coordinations and being monoanionic, dianionic or trianionic. Half-metallocene complexes with a four-membered chelating ring are focused on due to their unique dynamic behaviors of metal-centered racemization and chain transfer. The structural uniqueness of the metal complexes, the effects of the chelate ring sizes on their productivity and the activation processes of the metal complexes with cocatalysts are highlighted.

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INTRODUCTION

The development of single-site catalysts and catalyst precursors active in α -olefin polymerization is currently a highly popular topic in the field of polymer chemistry due to the high demand for well-defined poly(olefin)s in the petrochemical industry.¹ Since the development of Kaminsky's metallocene/methylaluminoxane (MAO) catalyst system, remarkable efforts in both academia and industry have been directed toward modifying the cyclopentadienyl (Cp) ligand architecture of metallocene-type complexes of group 4 metals to control their polymerization performance in terms of the molecular weight, molecular weight distribution, polymer microstructure and the monomer content of the copolymers.^{2–4} In addition, C_1 -, C_2 - and C_s -symmetric *ansa*-metallocene complexes have also been investigated for precise regulation of the polymer stereochemistry.⁵

Recent achievements have been ascribed to the use of various organic ligands containing heteroatoms as donors on supporting ligands at the metal centers of polymerization catalysts. A large number of non-metallocene complexes containing ligands with donors from all over the periodic table were prepared and tested as

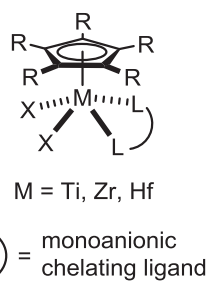
precatalysts for olefin polymerization.^{6–9} Between metallocene and non-metallocene catalysts, half-metallocene complexes proved to be unique catalysts due to their appropriately sized open coordination site.¹⁰ In particular, the constrained geometry catalysts of titanium, which produce highly branched polyethylene (PE) by ethylene polymerization, inspired polymer chemists to design and prepare various types of bridging and non-bridging half-metallocene complexes with monodentate supporting ligands on combination with Cp or its derivatives.¹¹ For bridging half-metallocene complexes, the coordination sphere can be tuned by modifying the bridging spacer. For example, a short bridging spacer opens more vacant sites for approaching monomers to the metal center. In contrast, the monomer coordination site is more flexibly tuned by using a non-bridged half-metallocene structure due to the wide applicability of the additional ancillary ligands. In this review, we provide an overview of the recent development of non-bridged half-metallocene complexes of group 4–6 metals supported by multidentate ligands and their catalytic behavior for the polymerization of α -olefins. In these reactions, ancillary ligands such as monoanionic amido, aryloxo and sulfido ligands have crucial roles not only for increasing catalytic

activity but also for controlling the microstructure of poly(ethylene) and poly(olefins).

HALF-METALLOCENE GROUP 4 METAL COMPLEXES WITH MONOANIONIC FOUR-MEMBERED CHELATING RINGS

Half-metallocene complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{MX}_2(\text{L}^\wedge\text{L})$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; L^\wedgeL = monoanionic chelating ligands) are representative structural motifs for mixed-ligated half-metallocene complexes (Scheme 1). Among the wide variety of $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{L}^\wedge\text{L})\text{X}_2$ complexes, half-metallocene complexes with a four-membered chelating ring have been extensively investigated because of the availability of various amidinate, guanidinate and iminophosphoramidate ligands. This section reviews half-metallocene catalysts that have anionic chelating ligands, which form four-membered chelating rings.

The first examples of such structural units are a series of half-metallocene complexes of group 4 metals with N,N' -bis(trimethylsilyl)- or N,N' -bis(aryl)benzamidinate ligands (Figure 1).^{12–16} The benzamidinate-supported complexes $(\eta^5\text{-C}_5\text{R}_5)\text{ZrX}_2[\text{NR}^1\text{C}(\text{Ph})\text{NR}^1]$ (**1a–d**) ($\text{X} = \text{Cl}, \text{Me}, \text{CH}_2\text{Ph}$) are active in the polymerization of ethylene on the addition of excess MAO, $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$; however, their catalytic activities are rather low (up to $60 \text{ kg-PE} (\text{mol cat})^{-1} \text{ h}^{-1} \text{ atm}^{-1}$). Collins and co-workers¹⁷ prepared half-metallocene zirconium complexes $\text{CpZrCl}_2[(\text{R}^2)_2\text{P}(\text{NR}^1)_2]$ (**2a–b**) with iminophosphoramidate ligands by the reaction of $\text{CpZr}(\text{NMe}_2)_3$ with the corresponding iminophosphoramidate and subsequent chlorination using $[\text{Me}_2\text{NH}][\text{HCl}]$ (Figure 1). The ethylene polymerization activity was low on activation with MAO at 50°C , because MAO could not sufficiently methylate the catalyst precursors **2a–b** at a low temperature. In contrast, at elevated temperatures, **2a–b**/MAO or **2a–b**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ /MAO exhibited higher catalytic activity and produced PE up to $180 \text{ kg-PE} (\text{mol cat})^{-1} \text{ h}^{-1} \text{ atm}^{-1}$.



Scheme 1 Structural motif of $(\eta^5\text{-C}_5\text{R}_5)\text{MX}_2(\text{L}^\wedge\text{L})$.

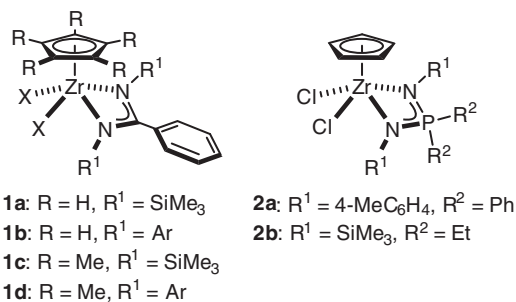
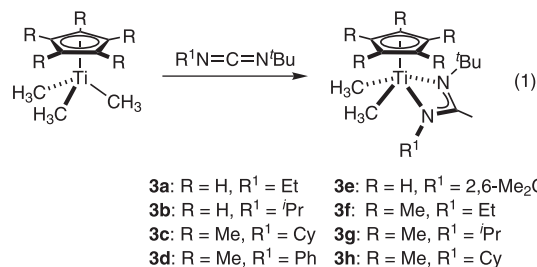


Figure 1 Half-zirconocene complexes, **1a–d** and **2a–b**, with monoanionic benzamidinate and iminophosphoramidate ligands.



The most remarkable contribution was Sita's half-metallocene complexes of group 4 metals with asymmetric acetamidinate ligands. Typically, the $(\eta^5\text{-C}_5\text{R}_5)\text{TiMe}_2[\text{NR}^1\text{C}(\text{Me})\text{N}^t\text{Bu}]$ (**3a–h**) complexes are prepared by the reaction of $(\eta^5\text{-C}_5\text{R}_5)\text{TiMe}_3$ with asymmetric carbodiimides, $\text{R}^1\text{N}=\text{C}=\text{N}^t\text{Bu}$, through insertion of the carbodiimides into metal–carbon bonds to form η^3 -acetamidinate moieties (equation 1).^{18–20} The corresponding zirconium and hafnium complexes are similarly prepared. Titanium complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{TiMe}_2[\text{NR}^1\text{C}(\text{Me})\text{NR}^2]$ (**3a–h**) had moderate catalytic activity (up to $22 \text{ kg} (\text{mol cat})^{-1} \text{ h}^{-1} \text{ atm}^{-1}$) for the polymerization of ethylene on activation with MAO.¹⁸ In contrast, the zirconium complexes **4a–c** and **5a–c** were effective catalysts for the polymerization of α -olefins and non-conjugated dienes (Figure 2). For example, the dimethylzirconium complexes **4a** and **4b** initiate the living polymerization of 1-hexene with a narrow molecular weight distribution after activation with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$. The stereochemistry of poly(1-hexene) is controlled by selecting the symmetry of the half-zirconocene precursors. In fact, the C_1 -symmetric half-zirconocene complex **4b**, which has different substituents attached to the nitrogen atoms of the acetamidinate ligand, catalyzed the stereospecific living polymerization of 1-hexene at -10°C to give *isotactic*-rich poly(1-hexene) ($M_w/M_n = 1.03$, $[\text{mmmm}] > 95\%$).²⁰ Furthermore, in the presence of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, the zirconium complexes **5a–c** catalyzed the polymerization of vinylcyclohexane at -10°C to give poly(vinylcyclohexane) with a very narrow molecular weight distribution ($M_w/M_n = 1.04\text{--}1.10$). It is noteworthy that all of the polymers were highly *isotactic* ($[\text{mmmm}] > 95\%$) even when the C_s -symmetric precatalysts **5a** and **5b** were used in the presence of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, suggesting that the polymerization proceeded via a typical chain-end controlled mechanism. The living polymerization ability of **4a–c** and **5a–c** was further utilized for the synthesis of block polymers. Complex **5b** combined with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ polymerized both 1-hexene and vinylcyclohexane in a living manner to produce triblock poly(vinylcyclohexane)-poly(1-hexene)-poly(vinylcyclohexane) with

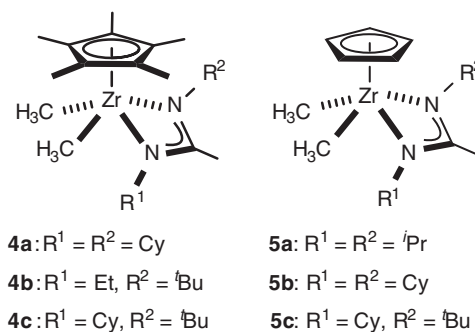


Figure 2 Acetamidinate-supported half-metallocene zirconium complexes for the living polymerization of α -olefins and non-conjugated dienes.

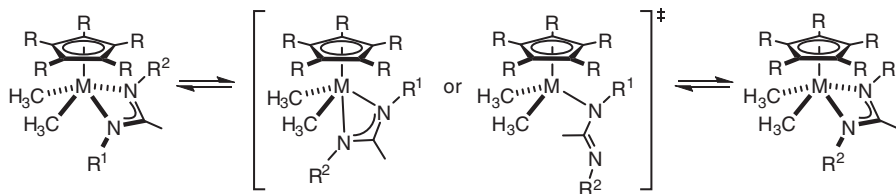


Figure 3 Metal-centered racemization through ligand dynamics.

Table 1 Barriers to racemization at the coalescence temperature for $(\eta^5\text{-C}_5\text{R}_5)\text{TiMe}_2[\text{N}^i\text{BuC}(\text{Me})\text{NR}^1]^{18}$

Entry	R	R ¹	Complex	ΔG_c^\ddagger (kcal mol ⁻¹)	T _c (K)
1	H	Et	3a	12.1	243
2	H	<i>i</i> Pr	3b	13.7	283
3	H	Cy	3c	14.7	283
4	H	Ph	3d	11.0	223
5	H	2,6-Me ₂ C ₆ H ₃	3e	12.6	233
6	Me	Et	3f	14.9	308
7	Me	<i>i</i> Pr	3g	14.1	295
8	Me	Cy	3h	15.2	293

Table 2 Effect of the substituents on the central amidinate carbon atom in the polymerization of 1-hexene by $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2[\text{N}^i\text{BuC}(\text{R})\text{NEt}][\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]^{26}$

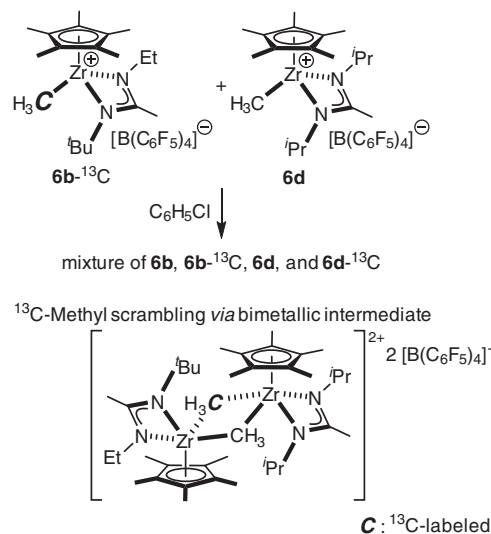
Entry	R	Yield (%)	M _n	M _w /M _n
1	Me	95	19 800	1.03 ^a
2	H	45	20 100	1.59
3	Ph	90	19 300	1.02 ^b
4	^t Bu	Trace	—	—

^aHigh isotacticity.

^bLow isotacticity.

an *isotactic*-rich poly(vinylcyclohexane) segment after sequential addition of the corresponding monomers.²¹ In addition, the complexes **4a–c** acted as catalyst precursors for the cyclopolymerization of non-conjugated dienes, such as 1,5-hexadiene, to produce poly(methylene-1,3-cyclopentane) with a high *trans* ring content (up to 82% *trans* content) and a high degree of *isotacticity*.²²

The most important fundamental aspect of the dissymmetric bidentate acetamidinate ligands attached to $(\eta^5\text{-C}_5\text{R}_5)\text{M}$ fragments is their ability to racemize the stereogenic metal center in neutral dialkyl complexes through either (1) a four-coordinated intermediate by the dissociation of one nitrogen donor (ligand-dissociation process) and/or (2) a five-coordinated distorted trigonal bipyramidal intermediate (ligand-flipping process), as schematically shown in Figure 3.^{18,19,23–25} Because the racemization of $(\eta^5\text{-C}_5\text{R}_5)\text{MMe}_2[\text{NR}^1\text{C}(\text{Me})\text{NR}^2]$ ($\text{R}^1 \neq \text{R}^2$) complexes proceeds at a range of temperatures on the NMR (nuclear magnetic resonance) time scale, a barrier for the racemization at the metal center has been estimated. For example, barriers for the racemization at the coalescence temperature (223–308 K) of the titanium complexes $(\eta^5\text{-C}_5\text{R}_5)\text{TiMe}_2[\text{NR}^1\text{C}(\text{Me})\text{NR}^2]$ (**3a–h**) are in the range of 11.0–



Scheme 2 Scrambling of a labeled methyl group in cationic zirconium complexes.

15.2 kcal mol⁻¹, showing that metal-centered racemization proceeds under mild conditions (Table 1).¹⁸ In addition, the barrier of the metal-centered racemization is not only influenced by the substituents on the Cp ring and nitrogen atoms of the amidinate ligands but also by the distal substituent on the central carbon of the amidinate ligands, allowing for the living and *isotactic* polymerization of 1-hexene by tuning the substituents on the amidinate ligands (Table 2).²⁶

To determine the mechanism, the cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}[\text{N}^i\text{BuC}(\text{Me})\text{NEt}][\text{B}(\text{C}_6\text{F}_5)_4]]$ (**6b**) was prepared by treating **4b** with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$. Because the metal center of **6b** was coordinatively unsaturated, its dimerization proceeded easily in the absence of Lewis bases to form a methyl-bridged dimeric complex, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}[\text{N}^i\text{BuC}(\text{Me})\text{NEt}]]_2(\mu\text{-Me})_2[\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**[6b]₂**). In solution, the monomer–dimer equilibrium between **6b** and **[6b]₂** and the exchange of the methyl groups bound to the zirconium atom were very rapid. Eventually, a mixture of a ¹³C-labeled cationic methyl complex (**6b-¹³C**) and a non-labeled cationic methyl complex with the *N,N'*-diisopropylacetamidinato ligand (**6d**) resulted in the fully ¹³C-scrambled mixture **6b**, **6b-¹³C**, **6d** and **6d-¹³C** (Scheme 2). Accordingly, it can be assumed that a polymer chain exchange reaction between active and/or dormant metal centers proceeds in the same manner.^{27,28}

To confirm metal-centered racemization during the polymerization reaction, a neutral dialkyl complex and a cationic alkyl complex were mixed to determine whether a degenerative living polymerization proceeded (Figure 4).^{25,29–31} A living polymerization is considered degenerative if reversible deactivation occurs during polymerization, that is, if the dormant species forms reversibly. The aforementioned

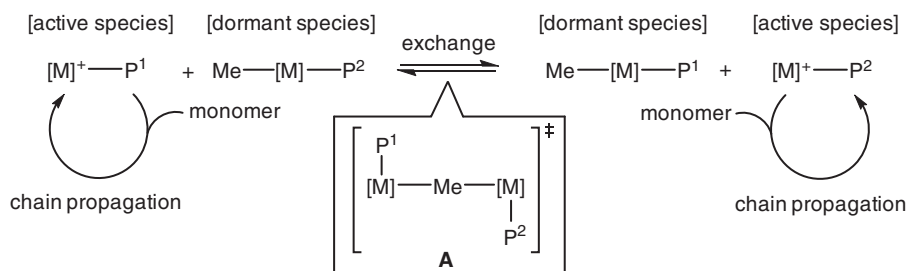
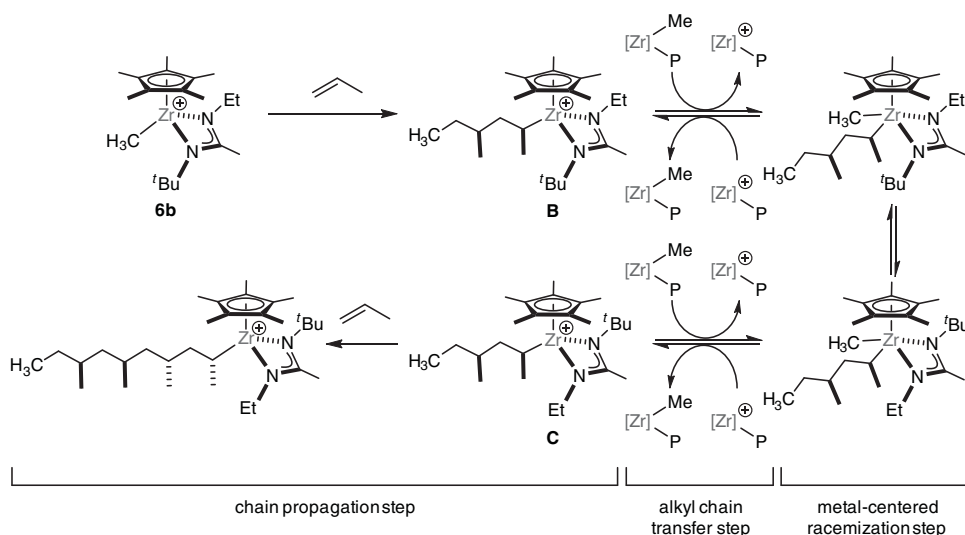


Figure 4 Conceptual scheme for degenerative living polymerization.²⁵



Scheme 3 Synthesis of isotactic polypropene with *mmrm* stereoerror through degenerative transfer living polymerization with $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2[\text{N}^t\text{BuC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ as a catalyst precursor. A full color version of this figure is available at *Polymer Journal* online.

test reaction was a 1:1 mixture of the cationic methylzirconium species $[\text{Zr}]^+-\text{Me}$ (**6b**) and the neutral dimethylzirconium complex $\text{Me}-[\text{Zr}]-\text{Me}$ (**4b**), to which monomers such as propene were added. As schematically outlined in Figure 4, the cationic methyl-zirconium species **6b** reacted with propene to afford $[\text{Zr}]^+-\text{P}$, and a subsequent alkyl exchange reaction between $[\text{Zr}]^+-\text{P}$ and $\text{Me}-[\text{Zr}]-\text{Me}$ produced an additional $[\text{Zr}]^+-\text{Me}$ and a dormant dialkyl species, $\text{P}-[\text{Zr}]-\text{Me}$, through monocationic μ -alkyl dimeric species A. The entire polymerization process is schematically shown in Scheme 3. The initial cationic catalyst **6b** afforded the cationic active species $[\text{Zr}]^+-\text{P}$ (**B**) with an *isotactic* polypropene block after the addition of a monomer. A subsequent alkyl exchange reaction between $[\text{Zr}]^+-\text{P}$ and $\text{Me}-[\text{Zr}]-\text{P}$ produced an additional $[\text{Zr}]^+-\text{P}$ and a dormant dialkyl species, $\text{P}-[\text{Zr}]-\text{Me}$, through a monocationic μ -alkyl dimeric species A, as described in Figure 4. The dormant methyl-polymeryl species, $\text{P}-[\text{Zr}]-\text{Me}$, was then racemized, and subsequent demethylation by other cationic alkyl species produced cationic alkyl species with different configuration, leading to the formation of isotactic polymeryl chains with *mmrm* stereoerror (Scheme 3). The frequency of the stereoerror in the polypropenes is controllable by changing the amount of the borate activator, leading to a different concentration of neutral dialkylzirconium species. A series of bimetallic complexes with linking amidinate ligands, $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2][\text{N}^t\text{BuC}(\text{Me})\text{N}](\text{CH}_2\text{CH}_2)_n[\text{NC}(\text{Me})\text{N}^t\text{Bu}][(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2]$ (**7a-c** in Figure 5), were investigated in association with the degenerative transfer living polymerization.³² Shorter linkers, that is, keeping the two metal centers in close proximity, led to an increased energy barrier for epimerization due to

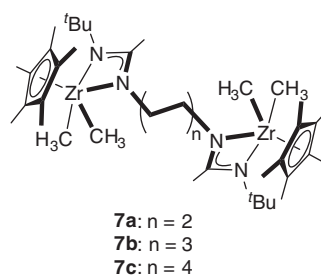
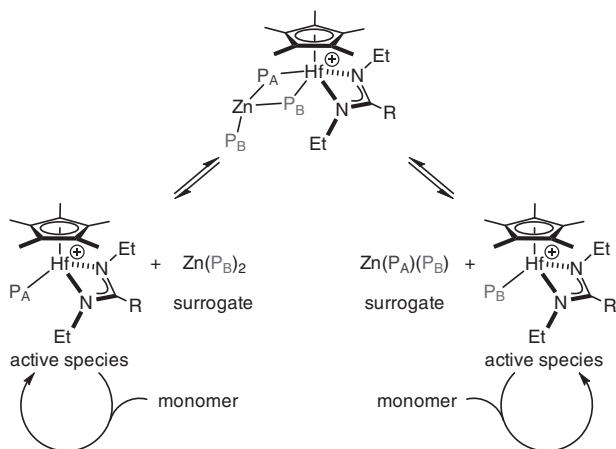


Figure 5 Bimetallic zirconium complexes supported by linked acetamidinate ligands.

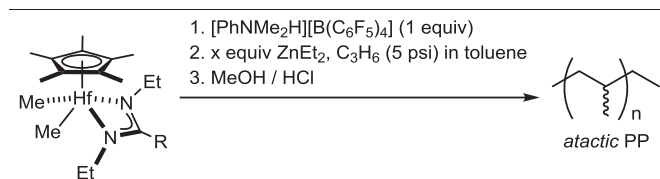
steric interactions, and therefore resulted in a smaller degree of stereoerror in the polymer.

Steric congestion around the metal center is another important factor. For example, the *N,N*-diethylacetamidinate-supported half-metallocene complexes of hafnium exhibit a unique behavior in the chain transfer polymerization of α -olefins in combination with excess amounts of main group metal alkyl reagents such as ZnEt_2 and AlR_3 ($\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, ^t\text{Bu}$). Main group alkyls serve as 'surrogate' metal sites because the chain transfer between the hafnium center and the main group alkyls is reversible, leading to the formation of main group metal compounds with growing polymer chains (Scheme 4). Typically, when $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]$ is activated by 1 equiv $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ under a propene atmosphere in the presence of different amounts of ZnEt_2 , the molecular weight of the



Scheme 4 Living coordinative chain transfer polymerization of α -olefins by $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ and ZnR_2 .³⁴ A full color version of this figure is available at *Polymer Journal* online.

Table 3 Living coordinative chain transfer polymerization of propene by $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ and ZnR_2 .³³

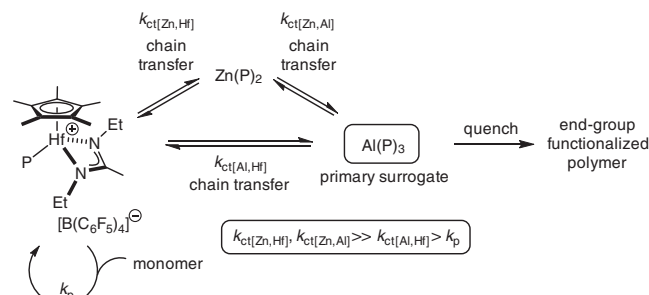


Run	ZnEt ₂ (equiv)	Yield (g)	M _n (× 10 ³)	M _w /M _n
1	200	4.99	1.45	1.08
2	100	4.93	2.28	1.06
3	50	4.94	4.18	1.04
4	20	4.18	8.75	1.04
5	10	4.78	18.7	1.04
6	5	4.85	33.3	1.09

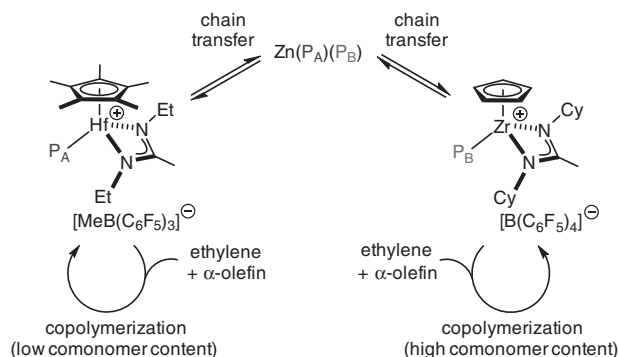
Abbreviation: equiv, equivalent.
Conditions: catalyst (20 μmol), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (20 μmol) and propene (5 p.s.i.) in toluene (total volume, 20 ml) for 2 h. ZnEt_2 was added as 1.1 M toluene solution.

polymer is highly dependent on the ratio of the hafnium precatalyst and ZnEt_2 (Table 3).^{33–35} Decreasing the amount of ZnEt_2 results in an increase in the molecular weight of the polypropene while maintaining the catalytic activity and narrow molecular weight distribution ($M_w/M_n < 1.10$).

Furthermore, ZnEt_2 mediates the reversible transfer of polymer chains between the catalytically active hafnium center of $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ and trialkylaluminum reagents (such as Al^iBu_3) as a primary surrogate (Scheme 5). In this ternary, living, coordinative chain transfer polymerization, it is notable that the addition of Al^iBu_3 reduced the required amount of ZnEt_2 . In this approach, a variety of end-functionalized polyolefins was accessible after appropriately quenching the polymer-bound aluminum species.³⁶ As ZnEt_2 mediated the reversible chain transfer between the two catalytically active metal centers of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(\text{R})\{\text{NEtC}(\text{Me})\text{NEt}\}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\text{R})\{\text{NCyC}(\text{Me})\text{NCy}\}][\text{B}(\text{C}_6\text{F}_5)_4]$, a unique ‘chain-shuttling’ polymerization occurred between hafnium and zirconium catalysts, producing poly(ethylene-co- α -olefin)s with different segments of α -olefin incorporation (Scheme 6).³⁷ Thus, such dynamic,



Scheme 5 Ternary living coordinative chain transfer polymerization of α -olefins by $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{ZnR}_2/\text{AlR}_3$.³⁶



Scheme 6 Living coordinative chain transfer polymerization of α -olefins by $(\eta^5\text{-C}_5\text{Me}_5)\text{HfMe}_2[\text{NEtC}(\text{Me})\text{NEt}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/(\eta^5\text{-C}_5\text{H}_5)\text{ZrMe}_2[\text{NCyC}(\text{Me})\text{NCy}]/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ and ZnR_2 .³⁷ A full color version of this figure is available at *Polymer Journal* online.

bimolecular chain transfer processes have been systematically applied to these half-metallocene amidinate complexes, leading to the production of new types of polyolefin materials. Controlling the dynamic processes between catalysts or a catalyst and main group metal alkyls by changing the different molar ratio of activator or different main group elements enable us to produce many materials, such as stereoblock and stereogradient polymers, from one catalyst.³⁸

HALF-METALLOCENE GROUP 4 METAL COMPLEXES WITH MONOANIONIC FIVE- AND SIX-MEMBERED CHELATING RINGS

Half-metallocene complexes with five- and six-membered chelating rings have been less explored compared with those bearing a monoanionic four-membered chelating ring, presumably due to the suppressed reactivity caused by the steric effects of the five- and six-membered chelating rings. Nonetheless, several precatalysts active in α -olefin polymerization have been reported to date.

Group 4 metal complexes bearing both Cp and pyridylalkoxide ligands were the first reported examples of half-metallocene complexes with monoanionic five-membered chelating rings (Figure 6).³⁹ Dichloride complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{M}\{\text{NC}_5\text{H}_4(\text{CR}_2\text{O})\text{-2}\}\text{Cl}_2$ (**8a**: M = Ti, R = ⁱPr; **8b**: M = Ti, R = Ph; **9a**: M = Zr, R = ⁱPr; **9b**: M = Zr, R = Ph), were prepared by the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_3$ with the lithium salt of the corresponding ligands. Complexes **8a**

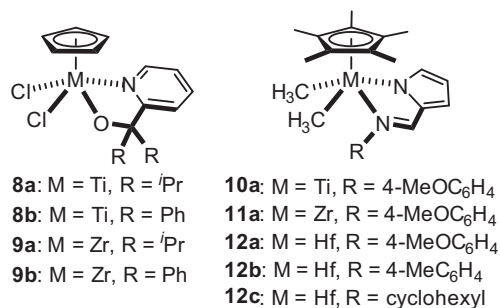


Figure 6 Half-metallocene complexes of group 4 metals with pyridylalkoxy and iminopyrrolyl ligands.

Table 4 Polymerization of 1-hexene catalyzed by (η^5 -C₅Me₅)Hf(R-pyr)Me₂ (**11**)/[Ph₃C][B(C₆F₅)₄]⁴⁵

Run	Cat.	R	Temp. (°C)	Time (h)	M _n ($\times 10^3$)	M _w /M _n	[mmmm] (%)
1	12a	4-MeOC ₆ H ₄	25	1.5	14.1	1.28	66
2	12a	4-MeOC ₆ H ₄	25	3	13.0	1.45	65
3	12a	4-MeOC ₆ H ₄	0	3	33.1	1.09	76
4	12a	4-MeOC ₆ H ₄	-10	3	13.6	1.08	89
5	12a	4-MeOC ₆ H ₄	-20	6	23.5	1.07	89
6 ^a	12b	4-MeC ₆ H ₄	25	3	(9.10/ 0.60)	(1.40/ 1.14)	43
7	12b	4-MeC ₆ H ₄	0	3	29.4	1.08	84
8	12b	4-MeC ₆ H ₄	-20	6	22.5	1.07	90
9	12c	Cyclohexyl	25	3	5.90	1.42	39
10	12c	Cyclohexyl	0	3	12.6	1.12	73
11	12c	Cyclohexyl	-20	6	9.00	1.08	75

Abbreviations: Cat., catalyst; Temp., temperature.

Conditions: catalyst (20 μ mol), [Ph₃C][B(C₆F₅)₄] (20 μ mol) and 1-hexene 1.25 ml (10 mmol) in C₆H₅Cl (2.75 ml).

^aBimolecular weight distribution.

and **8b** exhibited moderate activity (16–140 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) in the polymerization of ethylene in the presence of excess MAO. We investigated the α -olefin polymerization performance of group 4 metal complexes with iminopyrrole ligands.^{40–44} Treatment of (η^5 -C₅Me₅)MMe₃ with (*N*-alkyl/aryl-iminomethyl)pyrroles afforded various half-metallocene dimethyl complexes (**10a**, **11a**, **12a–c**) with five-membered dissymmetric chelating iminopyrrolyl ligands (Figure 6).^{45,46} Among the series of (η^5 -C₅Me₅)M(R-pyr)Me₂ (R-pyr = (*N*-alkyl/aryl-iminomethyl)pyrrolyl) complexes, the hafnium complexes (η^5 -C₅Me₅)Hf(R-pyr)Me₂ (**12a–c**) produced *isotactic* poly(1-hexene) on activation with [Ph₃C][B(C₆F₅)₄] (Table 4). The molecular weights of the poly(1-hexene)s obtained from **12a**/[Ph₃C][B(C₆F₅)₄] at 25 °C were almost constant when the reaction time was extended, and the ¹H NMR spectra of the resulting poly(1-hexene)s showed resonances corresponding to internal alkene protons, suggesting that β -H elimination was the terminal step (runs 1 and 2). Notably, the same polymerization conditions for **12a–c**/[Ph₃C][B(C₆F₅)₄] below 0 °C produced poly(1-hexene)s with very narrow molecular weight distributions ($M_w/M_n < 1.10$), and no alkenes formed in the polymer chain, suggesting a living polymerization (runs 3–5, 7, 8 and 11). Substituents on the imine-nitrogen atom of the ligand enhanced the catalytic activity and increased the *isotacticity* of the polymers. The *isotacticity* of poly(1-hexene)s obtained from **12c**/[Ph₃C][B(C₆F₅)₄] was moderately high due to the relatively fast racemization rate

Table 5 Activation parameters for the racemization process of (η^5 -C₅Me₅)M(4-MeOC₆H₄-pyr)Me₂ (**10a–12a**)⁴⁶

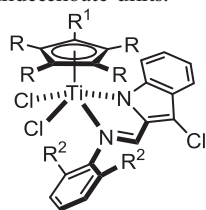
M	T _c (K)	ΔG_c^\ddagger (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹)	Mode
Ti (10a)	353	17.4	24.9 ± 0.4	21.2 ± 1.2	B
Zr (11a)	233	11.2	9.0 ± 0.3	-9.2 ± 0.3	A
Hf (12a)	268	13.0	12.4 ± 0.7	-3.4 ± 2.6	A

around the catalytically active metal center compared with **12a** and **12b** (runs 5 and 8 vs 11).

Because the iminopyrrolyl complexes **10a**, **11a** and **12a** exhibit fluxional behavior due to site-exchange racemization similar to the process of the four-membered system shown in Figure 3, the thermodynamic parameters of the racemization were estimated by variable temperature NMR measurements. The ring-flipping mechanism (mode **A**) occurs through a distorted trigonal-bipyramidal intermediate, whereas the ligand-dissociation mechanism (mode **B**) proceeds through a three-legged piano-stool geometry after dissociation of the imine moiety. The positive ΔS^\ddagger value of **10a** assignable to a ligand-dissociation mechanism (mode **B**) is ascribed to both the small ionic radii of titanium and the large chelating ring. In contrast, zirconium and hafnium favor a five-coordinated trigonal-bipyramidal intermediate (mode **A**), as confirmed by the negative ΔS^\ddagger values for the racemization process (Table 5).

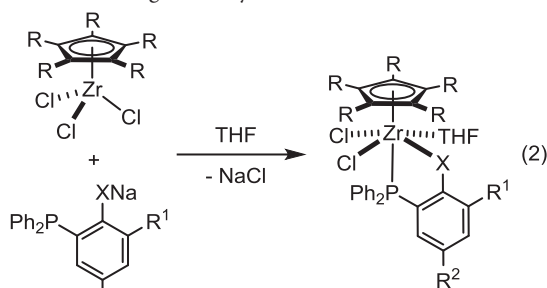
The half-titanocene complexes **13a–g** bearing iminoindole ligands were synthesized by treating (η^5 -C₅R₅)TiCl₃ (R = H, Me) or (η^5 -C₅H₄Me)TiCl₃ with the sodium salts of iminoindole ligands. The catalytic activity of the complexes was tested for the polymerization of ethylene and copolymerizations of ethylene/1-hexene and ethylene/methyl 10-undecanoate.⁴⁷ On activation with MAO (100 equiv), the titanium complexes with a Cp ligand showed moderate activity (152–512 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹). The corresponding titanium complexes with methyl-substituted Cp ligands exhibited even lower catalytic activity (up to 88 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) due to the steric hindrance of the substituted Cp ligands. It is noteworthy that the copolymerization of ethylene and polar monomers, such as esters, was catalyzed by late transition metal catalysts because of their tolerance toward the ester functional group.⁴⁸ The copolymerization of ethylene and methyl 10-undecanoate was catalyzed by complexes **13a–g**, which are the first examples of early transition metal catalysis. In this catalytic system, however, pretreatment of methyl 10-undecanoate with alkylaluminum reagents was necessary for consistent reproducibility. Moreover, the

resulting poly(ethylene-co-methyl 10-undecenoate)s contained ~ 1 mol% of methyl 10-undecenoate units.



- 13a:** R = R¹ = H, R² = Me
13b: R = R¹ = H, R² = Et
13c: R = R¹ = H, R² = *i*Pr
13d: R = R¹ = H, R² = F
13e: R = R¹ = H, R² = Cl
13f: R = H, R¹ = Me, R² = F
13g: R = R¹ = Me, R² = F

The half-zirconocene complexes containing the phosphine-(thio)phenolate ligands (η^5 -C₅R₅)ZrCl₂(X[^]PPh₂)(THF) (**14**: R = H, Me; X = O, S) were synthesized by the reaction of (η^5 -C₅R₅)ZrCl₃ with the sodium salt of the phosphine-(thio)phenolate ligands (eq. 2).⁴⁹ The complexes **14a–i** adopt a six-coordinate, distorted octahedral geometry around the zirconium center with a five-membered chelating ring. Substituents on the aromatic ring of the phosphine-(thio)phenolate ligands affected the configuration of **14a–i**: the chalcogen donor occupied the equatorial position and the phosphorous atom of the chelating ligand was located at the axial site. In the presence of excess modified MAO (MMAO), these zirconium complexes (**14a–i**) were examined for use as catalysts for ethylene polymerization, and the results are summarized in Table 6. Substituents at the R¹ position affected the catalytic performance, and a trimethylsilyl group at the R¹ position clearly improved the catalytic activity compared with phenyl- and *tert*-butyl-substituted ligands. Changing the donor element from oxygen to sulfur slightly decreased the catalytic activity. The pentamethylcyclopentadienyl complexes **14a–e** showed lower activity and produced higher molecular weight polymers than the Cp-analogous **14f–i**, as the bulky (η^5 -C₅Me₅) ligand decelerated both the ethylene insertion and the chain transfer reaction. The Cp-based complexes **14f–i** were less bulky, therefore these complexes promoted the copolymerization of ethylene and 1-hexene with high activity.



- 14a:** R = Me, X = O, R¹ = Ph, R² = H
14b: R = Me, X = O, R¹ = *t*Bu, R² = H
14c: R = Me, X = O, R¹ = R² = *t*Bu
14d: R = Me, X = O, R¹ = SiMe₃, R² = H
14e: R = Me, X = S, R¹ = SiMe₃, R² = H
14f: R = H, X = O, R¹ = *t*Bu, R² = H
14g: R = H, X = O, R¹ = R² = *t*Bu
14h: R = H, X = O, R¹ = SiMe₃, R² = H
14i: R = H, X = S, R¹ = SiMe₃, R² = H

Table 6 Ethylene polymerization for (η^5 -C₅R₅)ZrCl₂(X[^]PPh₂)(THF)/MMAO⁴⁹

Run	Cat.	Yield (mg)	Activity		
			(kg-PE (mol cat) ⁻¹ h ⁻¹ atm ⁻¹)	M _w ($\times 10^3$)	M _w /M _n
1	14a	410	309	401	2.1
2	14b	480	360	651	2.6
3	14c	220	165	536	1.8
4	14d	1340	1005	427	2.2
5	14e	860	630	544	2.1
6	14f	1340	2010	258	2.3
7	14g	2690	4035	172	2.0
8	14h	1390	2085	200	2.1
9	14i	420	315	336	2.2

Abbreviation: Cat., catalyst.
 Conditions: MMAO as a cocatalyst (Al/Zr = 2000), 10 min, ethylene pressure = 4 atm, in toluene (total volume = 80 ml).

Selected half-metallocene complexes with six-membered chelating rings are depicted schematically in Figure 7.^{50–53} In 2003, Bochmann and Lancaster⁵⁰ reported the half-metallocene complexes of titanium and zirconium with phenoxy-imine (**15a–c** and **16a–c**) and phenoxy-amine ligands (**17–19**), which they prepared by treating (η^5 -C₅H₅)MCl₃ (M = Ti, Zr) with the lithium salts of phenoxy-imine and -amine ligands in tetrahydrofuran (THF), respectively. These complexes have a six-membered chelating ring, except for **19**, whose amine moiety dissociates from the metal center due to steric congestion in solution. Complexes **15–19** have moderate activity (2–210 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) for the polymerization of ethylene on combination with excess MAO. The catalytic activity of the phenoxy-imine complexes **15a–c** and **16a–c** is slightly higher than that of phenoxy-amine complexes **17–19**.

The β -enaminoketonato half-metallocene complexes of titanium (**20a–d**) were also prepared by reacting (η^5 -C₅H₅)TiCl₃ with the corresponding free ligand in the presence of NEt₃ as a base.⁵¹ The catalyst system **20a–d**/MMAO was active for the homopolymerization of ethylene and also for the copolymerization of ethylene and norbornene. As a result, an unexpected additive effect was observed: the addition of norbornene (~ 2000 equiv to Ti) to the reaction mixture improved the catalytic activity, and the resulting ethylene/norbornene copolymers had high molecular weights and relatively narrow M_w/M_n values (2.02–2.93). In contrast, a large excess of norbornene ($\sim 10\,000$ equiv to Ti) severely decreased the catalytic activity.

The half-metallocene complexes possessing phosphine oxide-(thio)phenolate ligands **21–23** exhibit moderate-to-high catalytic activity toward ethylene polymerization (up to 3320 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) on activation with a cocatalyst system of [Ph₃C][B(C₆F₅)₄] and Al^{*i*}Bu₃, yielding PE with a unimodal molecular weight distribution. A unique feature is that the best catalytic performance for each complex was observed at a high temperature (75 °C).^{52,53} Notably, **23a–g**, bearing only one chloride ligand, exhibited high catalytic activity after activation with MMAO. Similar catalytic behavior was also observed for the half-metallocene complexes **24** and **25**, which were supported by two phenoxy-imine ligands and one chloride ligand.^{54,55} Scheme 7 shows the activation process of monochloro complex **23b** by AlMe₃ according to DFT calculations. In the first stage, **23b** reacts with AlMe₃ to form the monomethyl species **A**. The subsequent reaction of **A** with AlMe₃ affords the Zr/Al species **B**. Next, the oxygen atom of the phenoxy moiety interacts with the additional AlMe₃ to form a μ -methyl-bridged heterobimetallic species. After π -complexation of

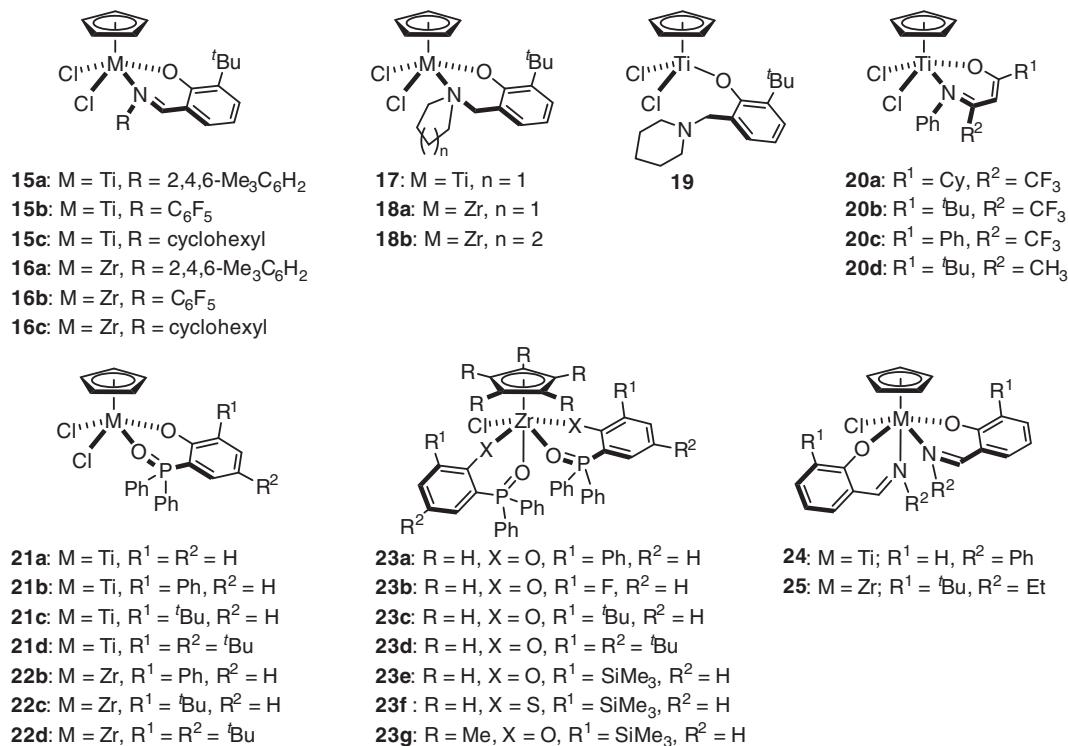
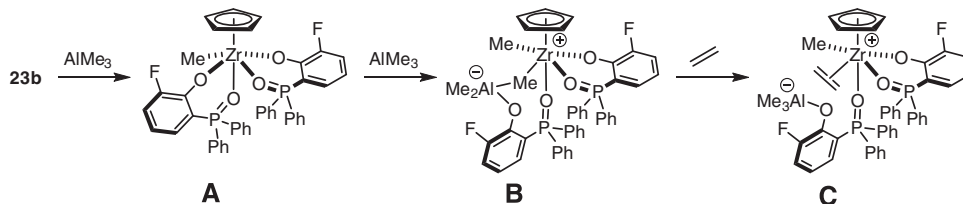


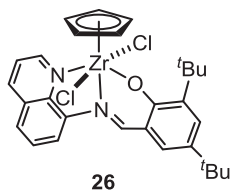
Figure 7 Half-metallocene complexes of titanium and zirconium with six-membered chelating rings.



Scheme 7 Proposed reaction pathway for generating catalytically active cationic alkyl species from the monochloro complex.

ethylene, dissociation of the weakly interacting AlMe₃ moiety from zirconium generates C. In relation to this mechanism, Stephan and co-workers⁵⁶ reported that an aryloxy ligand was removed from titanium when excess AlMe₃ was added to CpTi(OAr)₂Cl complexes, resulting in the transfer of one aryloxy ligand to the aluminum center and yielding CpTi(OAr)Me₂ and [Me₂Al]₂(μ-OAr)₂ complexes.

Tridentate ligand coordination to half-metallocene units provides another class of catalysts for olefin polymerization. A monoanionic quinoline-amino-phenolate tridentate ligand was introduced to a half-zirconocene complex to give **26**, which was comprised of both a five-membered and a six-membered chelating ring.⁵⁷ Complex **26** was active in the polymerization of ethylene on activation with excess MAO, and the best catalytic activity (403 kg-PE (mol cat)⁻¹h⁻¹atm⁻¹) was achieved at 75 °C in the presence of 1000 equiv MAO.



HALF-METALLOCENE GROUP 4 METAL COMPLEXES WITH MONOANIONIC THREE-MEMBERED CHELATING RINGS

Three-membered chelates are attractive structural motifs because there is little steric congestion around the reactive metal center. Monoanions of hydrazine, pyrazole, hydroxylamine and phosphinoamines were introduced to half-metallocene fragments as shown in Figure 8.^{58–61} Complexes **27a–c**, **28a–g** and **30a–c** possess a four-legged piano-stool geometry around the titanium atoms, whereas complexes **29a–f** adopt a trigonal bipyramidal geometry in which the (η^5 -C₅Me₅) ligand and a nitrogen atom occupy the axial positions. Ethylene polymerization activity of **27a–c** in the presence of excess MAO was low (up to 55 kg-PE (mol cat)⁻¹h⁻¹atm⁻¹), whereas η^2 -pyrazolato-coordinated complexes **28a–g** had high ethylene polymerization activity in combination with excess d-MAO. Among the (η^5 -C₅H₅) titanium complexes **28a–d** with η^2 -pyrazolato ligands, catalytic activity was improved by increasing the size of R¹ (R¹ = Ph (**28d**), up to 200 kg-PE (mol cat)⁻¹h⁻¹atm⁻¹). In contrast, the activity of the (η^5 -C₅Me₅) analogs **28e–g** was increased by decreasing the steric bulk on the η^2 -pyrazolato ligands (R¹ = H, up to 1500 kg-PE (mol cat)⁻¹h⁻¹atm⁻¹).

The η^2 -(N,O)-chelated hydroxyamino complexes **29a–f** were examined as precatalysts for the polymerization of propene in the presence of [Ph₃C][B(C₆F₅)₄]/Al(^tBu)₃. The propene polymerization

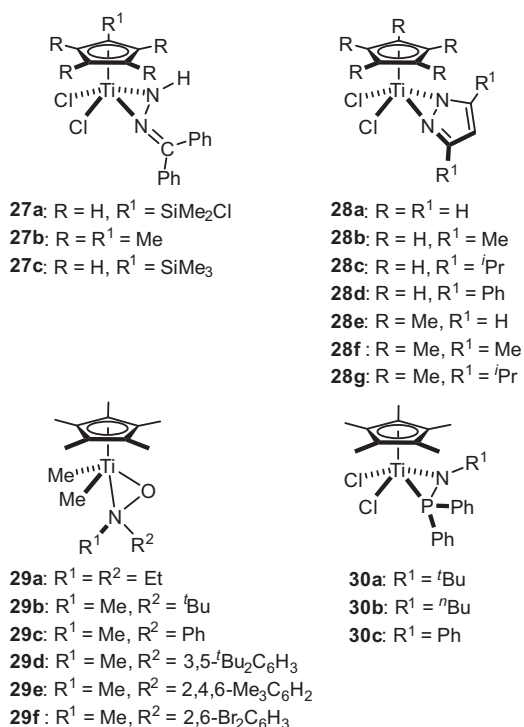


Figure 8 Half-metallocene complexes of titanium with three-membered chelating rings.

activity of **29a** was comparable to that of other metallocene and half-metallocene complexes of group 4 metals. The obtained polymers were *atactic* poly(propene)s with a narrow molecular weight distribution ($M_w/M_n \approx 2$). *N,N*-Dialkyl-substituted hydroxyaminato complexes **29a** and **29b** showed higher propene polymerization activity than the *N*-alkyl-*N*-aryl-substituted complexes **29c-f**. The cocatalyst had clear effects on the ethylene polymerization activity of the η^2 -(*N,P*)-chelated phosphinamide complexes **30a-c**. When MMAO was used as the cocatalyst, the catalytic activity was low (up to 64 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹), whereas the catalytic activity of **30a**[Ph₃C][B(C₆F₅)₄]/Al(^tBu)₃ was dramatically improved by changing the Ti/Al ratio. The highest activity was observed with Ti/Al = 1/200 (2516 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹).

HALF-METALLOCENE GROUP 4 METAL COMPLEXES WITH DIANIONIC AND TRIANIONIC CHELATING LIGANDS

The introduction of dianionic chelating ligands to half-titanocene fragments is distinctively featured by the formation of monochloro and monoalkyl complexes (Figure 9).⁶²⁻⁶⁴ The complexes **31-33** were active in the polymerization of ethylene and α -olefins in the presence of excess amounts of MAO or AlR₃/[Ph₃C][B(C₆F₅)₄]. To elucidate the activation step for the monochloro complex **31a**, we investigated the additive effect of the cocatalysts with **31b** for ethylene polymerization (Table 7).⁶² A mixture of **31a** and [Ph₃C][B(C₆F₅)₄] in the presence of Al(^tBu)₃ (100 equiv) showed the highest ethylene polymerization activity, indicating that the two components were indispensable in this catalyst-activation process. Otherwise, the catalytic activity of **31b** with only [Ph₃C][B(C₆F₅)₄] or Al(^tBu)₃ was very low (run 1 vs runs 6 and 7). Changing Al(^tBu)₃ to AlMe₃ almost completely suppressed the catalytic activity due to inefficient catalyst activation (run 2, *vide infra*). When complex **31a** was treated with

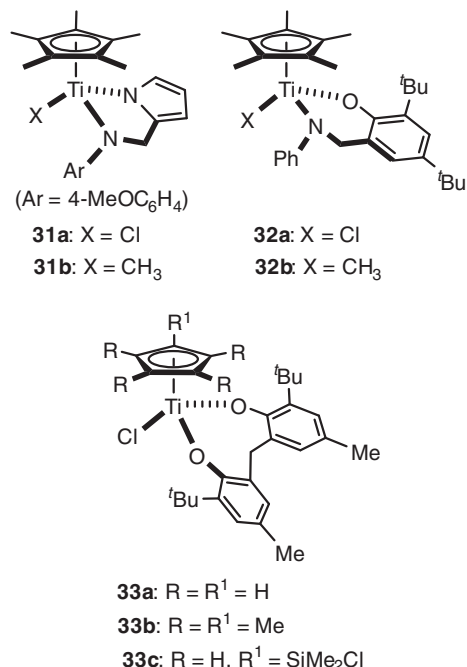


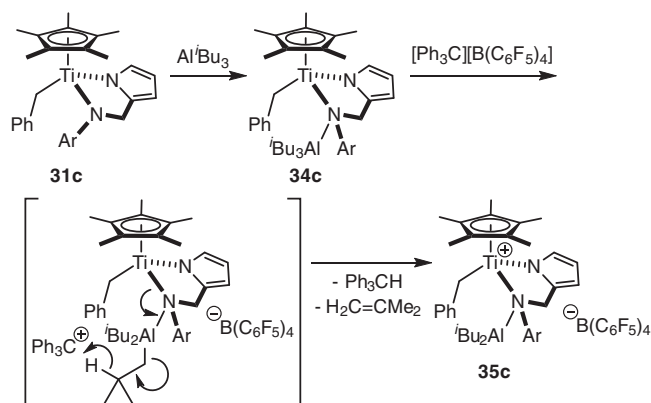
Figure 9 Half-metallocene complexes of titanium with dianionic bidentate ligands.

Table 7 Ethylene polymerization catalyzed by **31b**/cocatalyst⁶²

Run	Cocatalyst	Activity (kg-PE (mol cat) ⁻¹ h ⁻¹ atm ⁻¹)	M _w (× 10 ³)
1	[Ph ₃ C][B(C ₆ F ₅) ₄]/Al(^t Bu) ₃	327	250
2	[Ph ₃ C][B(C ₆ F ₅) ₄]/AlMe ₃	Trace	—
3	MMAO	111	— ^a
4	d-MMAO	135	— ^a
5	MAO	60	60
6	[Ph ₃ C][B(C ₆ F ₅) ₄]	0	—
7	Al(^t Bu) ₃	<1	—
8	Al(C ₆ F ₅) ₃	0	—

Conditions: ethylene pressure = 1 atm, in toluene ([catalyst] = 0.5 mm), temperature = 25 °C.
^aNot determined because of high molecular weight.

excess amounts of MAO, MMAO or dried MMAO (d-MMAO) under an ethylene atmosphere, the catalyst showed moderate activity (runs 3–5). The better catalytic activity of **31a**/MMAO and **31a**/d-MMAO may be attributed to the importance of an isobutyl group attached to the aluminum atom in the cocatalyst. On the other hand, a mixture of **31a** and Al(C₆F₅)₃ showed no ethylene polymerization activity (run 8). Therefore, the roles of both [Ph₃C][B(C₆F₅)₄] and Al(^tBu)₃ in the reaction with the benzyltitanium complex **31c** as the catalyst precursor were investigated. Scheme 8 shows a plausible pathway for the generation of the catalytically active species. The addition of Al(^tBu)₃ to **31c** resulted in the formation of the bimetallic species **34c**, where the amido-nitrogen atom of the pyrrolylamido ligand bridged the titanium and aluminum atoms. The subsequent reaction of **34c** with [Ph₃C][B(C₆F₅)₄] generated triphenylmethane, isobutene and the cationic benzyltitanium species **35c** through H abstraction from the isobutyl group attached to the aluminum atom. During the H abstraction reaction, the aluminum atom covalently bonded to the amido-nitrogen atom to form complex **35c**, which was active for further insertion of ethylene into the titanium–carbon bond. The low



Scheme 8 Al/Bu₃-mediated activation pathway for the generation of catalytically active cationic alkyl species.

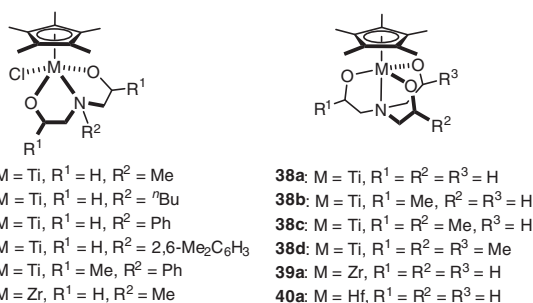
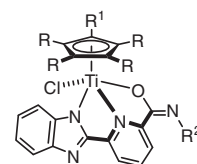


Figure 10 Half-metallocene complexes with ethanolamine-based multidentate ligands.

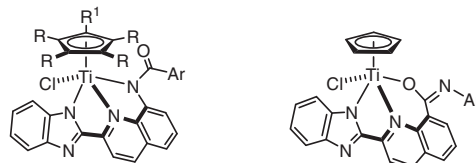
catalytic activity of **31b**/[Ph₃C][B(C₆F₅)₄]/AlMe₃ is rationally ascribed to the difficulty of abstracting H from the methyl group attached to the aluminum.

The dianionic tridentate ligands O[−]N[−]O[−] = NR²(CH₂CHR¹O)₂ and the trianionic tetradentate ligands N[−](O[−])₃ = N(CH₂CHR¹O)₃ were introduced to (η^5 -C₅Me₅)M fragments to give (η^5 -C₅Me₅)MCl(O[−]N[−]O[−]) (**36a–e** for M = Ti; **37a** for M = Zr) and (η^5 -C₅Me₅)M[(N[−]O[−])₃] (**38a–d** for M = Ti; **39a** for M = Zr; **40a** for M = Hf), respectively (Figure 10).^{65–71} The complexes **36a–e** and **37a** became active catalysts for ethylene polymerization on treatment with MMAO, although their catalytic activity was low (10–65 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}). The catalyst-activation pathway of these complexes with the aluminum cocatalyst has not yet been elucidated. The triethanolamine non-halide complexes **38a**, **39a** and **40a** exhibited much higher activities (for Ti: up to 740 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}, for Zr: up to 260 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}, for Hf: up to 42 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}) for ethylene polymerization in the presence of MAO, compared with the (η^5 -C₅Me₅)TiCl₃/MAO system.⁶⁶ The titanium complexes **38a–d** are reported to assist the syndiospecific polymerization of styrene.^{65,67–71}

Benzimidazolyl-based tridentate ligands were developed by Sun *et al.*, who prepared the half-titanocene complexes **41–43** (Figure 11) as catalyst precursors for ethylene polymerization and ethylene/ α -olefin copolymerization. The complexes **41a–g** bearing (η^5 -C₅H₅) or (η^5 -C₅H₄Me) and benzimidazolyl-pyridyl ligands were active (480–660 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}) for ethylene polymerization in the presence of excess MAO, whereas the same catalytic system was inactive in the ethylene/ α -olefin copolymerization.⁷² The methyl substituents on the Cp ring reduced the catalytic activity for



- 41a:** R = R¹ = H, R² = 2,6-Me₂C₆H₃
41b: R = R¹ = H, R² = 2,6-Et₂C₆H₃
41c: R = R¹ = H, R² = 2,6-ⁱPr₂C₆H₃
41d: R = R¹ = H, R² = 2,6-F₂C₆H₃
41e: R = R¹ = H, R² = 2,6-Cl₂C₆H₃
41f: R = R¹ = H, R² = ⁿBu
41g: R = H, R¹ = Me, R² = 2,6-Et₂C₆H₃
41h: R = R¹ = Me, R² = 2,6-Me₂C₆H₃
41i: R = R¹ = Me, R² = 2,6-Et₂C₆H₃
41j: R = R¹ = Me, R² = 2,6-ⁱPr₂C₆H₃
41k: R = R¹ = Me, R² = 2,6-F₂C₆H₃
41l: R = R¹ = Me, R² = 2,6-Cl₂C₆H₃
41m: R = R¹ = Me, R² = ⁿBu



- 42a:** R = R¹ = H, Ar = 4-MeOC₆H₄
42b: R = R¹ = H, Ar = 4-MeC₆H₄
42c: R = R¹ = H, Ar = Ph
42d: R = R¹ = H, Ar = 4-FC₆H₄
42e: R = R¹ = H, Ar = 4-ClC₆H₄
42f: R = R¹ = H, Ar = 4-BrC₆H₄
42g: R = H, R¹ = Me, Ar = 4-MeC₆H₄
42h: R = R¹ = Me, Ar = 4-MeC₆H₄
43a: Ar = 2,6-ⁱPr₂C₆H₃
43b: Ar = 2,6-Et₂C₆H₃
43c: Ar = 2,6-Me₂C₆H₃
43d: Ar = 2,4,6-Me₃C₆H₂
43e: Ar = Ph
43f: Ar = 2,6-F₂C₆H₃

Figure 11 Half-metallocene complexes with benzimidazolyl-based tridentate ligands.

complexes **41h–m** due to the steric protection around the relatively crowded metal center (140–300 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}). Furthermore, the amount of MAO strongly affected the catalytic activity. When 750 equiv MAO was applied to complex **41a**, PE was not obtained; however, PE production was improved (260 kg-PE (mol cat)^{−1} h^{−1} atm^{−1} at 80 °C) in the presence of 1500 equiv MAO. In addition, the catalytic activity was four times higher when 10 000 equiv MAO was used (1060 kg-PE (mol cat)^{−1} h^{−1} atm^{−1} at 80 °C). The complexes **42a–h** and **43a–f** catalyzed both ethylene homopolymerization and ethylene/ α -olefin copolymerization.^{73,74} In the case of ethylene polymerization with **42a–h** and **43a–f**, increasing the amount of MAO to 30 000 equiv and elevating the reaction temperature to 80 °C resulted in high catalytic activity (up to 650 kg-PE (mol cat)^{−1} h^{−1} atm^{−1}). Notably, **43a–f** furnished linear high-density PE with high T_m values (131–135 °C) and much higher molecular weights than those of PE obtained from **41a–m** and **42a–h**. The degree of 1-hexene or 1-octene incorporation in the ethylene/ α -olefin copolymers was controllable by changing the ligand substituents in **42a–h** and **43a–f**. Under identical copolymerization conditions with ethylene and 1-hexene, **42a–h**/MAO produced copolymers with ~2 mol% content of 1-hexene, whereas **43a–f**/MAO afforded higher amounts of 1-hexene incorporation for copolymers (up to 4.3 mol%).

HALF-METALLOCENE GROUP 5 METAL COMPLEXES WITH ANIONIC CHELATING LIGANDS

In the late 1960s, chloride and acetylacetonate complexes of vanadium were reported to be active for α -olefin polymerization on treatment with excess alkylaluminum reagents.^{75,76} Ligand architectures around the vanadium atom were extensively investigated for controlling

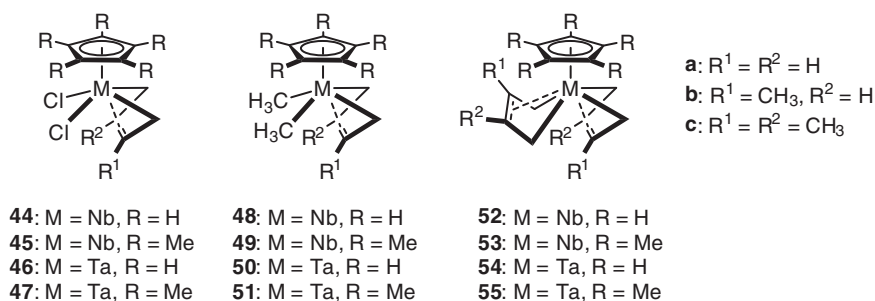


Figure 12 Half-metallocene complexes of niobium and tantalum with diene ligands.

stereoselectivity (2,1-insertion) and the living nature of polymerization.^{77–79} In contrast to the homoleptic complexes of vanadium, group 5 metal complexes bearing suitable organic ligands have been less developed, except for our reports on the half-metallocene complexes of niobium and tantalum with substituted butadiene, 1-azabutadiene and 1,4-diazabutadiene ligands.^{80–82}

Surprisingly, metallocene complexes of niobium and tantalum, $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$ (M = Nb, Ta), are catalytically inactive in the polymerization of ethylene, even when combined with excess MAO. Group 5 metal diene fragments, $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\eta^4\text{-diene})$, which are isoelectronic to $(\eta^5\text{-C}_5\text{R}_5)_2\text{M}$ (M = group 4 metals), are unique structural motifs that show catalytic activity in living ethylene polymerization, yielding PE with a very narrow molecular weight distribution.^{83,84} The catalyst precursors $(\eta^5\text{-C}_5\text{R}_5)\text{MCl}_2(\eta^4\text{-diene})$ (M = Nb (**44**: R = H, **45**: R = Me), Ta (**46**: R = H, **47**: R = Me)) and their dimethyl derivatives **48–51** were prepared by reacting $(\eta^5\text{-C}_5\text{R}_5)\text{MCl}_4$ with 1,3-diene compounds of magnesium in THF and methylating the corresponding complexes with 2 equiv MeMgI. By adding 2 equiv of the magnesium-diene reagents to $(\eta^5\text{-C}_5\text{R}_5)\text{MCl}_4$, the corresponding bis(diene) complexes of niobium and tantalum (**52–55**) were obtained (Figure 12).^{85–87}

The half-metallocene diene complexes of niobium and tantalum act as catalysts for living polymerization of ethylene in the presence of 500 equiv of MAO (Table 8). The dichloro- and dimethyl-tantalum complexes **47a** and **51a**/MAO exhibited almost the same catalytic activity, suggesting the formation of the same catalytically active cationic alkyl species in the reaction mixture (runs 10 and 11 vs 13 and 14). The structure of the diene ligands affected the catalytic activity. For example, niobium and tantalum complexes with 1,3-butadiene- or 2,3-dimethyl-1,3-butadiene-derived ligands had relatively high catalytic activity compared with complexes having a 2-methyl-1,3-butadiene-derived ligand (runs 3, 4 and 7). Methyl substituents on the Cp ligand stabilized the catalytically active species. At room temperature, the catalytic activity of the $(\eta^5\text{-C}_5\text{Me}_5)$ complex **47a** was higher than that of the $(\eta^5\text{-C}_5\text{H}_5)$ complex **46a** (runs 8 and 10). On the other hand, complex **46a** had higher catalytic activity at -20°C compared with the polymerization reaction conducted at room temperature, due to the low stability of the catalytically active cationic alkyl species derived from **46a** (runs 8 vs 9). Notably, the narrow molecular weight distribution ($M_w/M_n = 1.05\text{--}1.51$) of PE was obtained at -20°C by this series of niobium and tantalum complexes in the presence of MAO (500 equiv). In addition, the plot of the reaction time vs the molecular weight for PE obtained with **51a**/MAO revealed a linear relationship while maintaining a narrow molecular weight distribution, clearly demonstrating the living nature of the ethylene polymerization. Treatment of **51b** with $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 led to the formation of a cationic methyl species

Table 8 Ethylene polymerization catalyzed by $(\eta^5\text{-C}_5\text{R}_5)\text{MCl}_2(\eta^4\text{-diene})/\text{MAO}$ ⁸⁴

Run	Cat.	Temp. ($^\circ\text{C}$)	Activity		
			(kg-PE (mol cat) ⁻¹ h ⁻¹ atm ⁻¹)	$M_n (\times 10^3)$	M_w/M_n
1	45a	20	38.70	82.9	1.30
2	45a	0	14.50	49.5	1.07
3	45a	-20	10.65	23.6	1.05
4	45b	-20	1.02	5.10	1.09
5	45c	20	35.23	105.4	1.18
6	45c	0	21.87	81.6	1.08
7	45c	-20	12.71	41.0	1.05
8	46a	20	0.52	—	—
9	46a	-20	7.07	81.8	1.40
10	47a	20	5.93	20.3	2.04
11	47a	-20	1.51	20.3	1.16
12	47b	20	1.90	11.5	1.63
13	51a	20	4.48	20.4	2.06
14	51a	-20	1.18	25.5	1.08
15	53c	20	24.65	30.7	1.18
16	53c	0	21.95	28.2	1.13
17	53c	-20	12.48	14.2	1.06

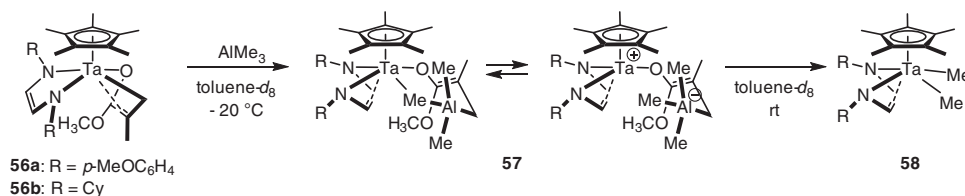
Abbreviations: Cat., catalyst; Temp., temperature.

Conditions: MAO as a cocatalyst (Al/M = 500), 6 h, ethylene pressure = 1 atm, in toluene (1.44×10^{-3} M of [Ta]).

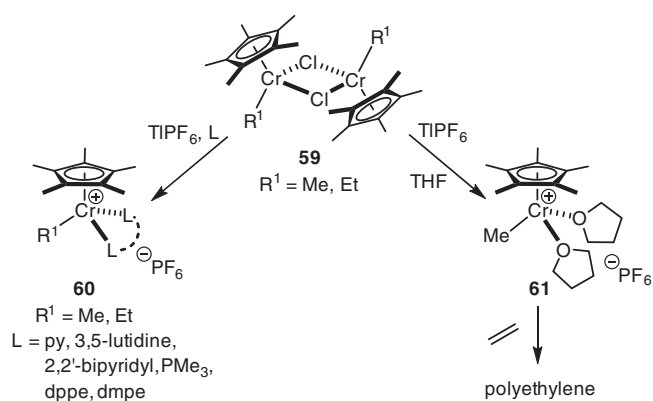
$[(\eta^5\text{-C}_5\text{Me}_5)\text{TaMe}(\eta^4\text{-isoprene})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ that was active for ethylene polymerization without any other additives. This species, however, had low catalytic activity.

When the bis(diene) complexes **52–55** were utilized as catalyst precursors, the catalytic activity was essentially the same as that of the corresponding mono(diene) complexes (runs 5–7 vs 15–17). On the basis of the M_n and M_w/M_n values of the PE obtained from **45c** and **53c**, the initiation efficiency of **53c** was higher (78–92%) than that of **45c** (27–34%). This result was consistent with the stability of the diene-coordinated aluminum species generated during the activation by MAO.

Some metallocene complexes of group 3 and group 4 metals initiate living polymerization of methyl methacrylate (MMA) and methyl acrylate to yield syndiotactic polymers.⁸⁸ Furthermore, half-metallocene tantalum complexes containing two-electron-reduced N,N' -disubstituted-1,4-diaza-1,3-butadiene and MMA ligands (**56**) were reported to act as catalyst precursors for MMA polymerization in the presence of 1 equiv of AlMe_3 as the cocatalyst.⁸⁹ Polymerization below 0°C produced syndiotactic-rich poly(MMA) in a high yield with a narrow molecular weight distribution ($M_w/M_n = 1.2$). The molecular weight of poly(MMA) linearly increased with consumption of the monomer, indicating living



Scheme 9 Activation pathway for the generation of the catalytically active tantalum-enolate species.



Scheme 10 Half-chromocene complexes as ethylene polymerization catalysts.

Table 9 Ethylene polymerization for (η^5 -C₅Me₅)CrCl[2,4-^tBu₂-6-(CH = NR)₆H₂O]/AlR₃¹⁰⁶

Run	Cat.	AlR ₃	Cr/Al	Activity (kg-PE (mol cat) ⁻¹ h ⁻¹ atm ⁻¹)	M _n (× 10 ³)
1	63a (5 μmol)	AlMe ₃	1/25	809	1010
2	63a (5 μmol)	AlMe ₃	1/50	755	1060
3	63a (5 μmol)	AlMe ₃	1/100	409	1100
4	63a (5 μmol)	AlEt ₃	1/25	341	1200
5	63a (10 μmol)	Al ⁱ Bu ₃	1/25	63	1090
6	63b (10 μmol)	AlMe ₃	1/25	422	1260
7	63b (10 μmol)	AlMe ₃	1/100	170	1100
8	63c (10 μmol)	AlMe ₃	1/25	65	1450
9	63c (10 μmol)	AlMe ₃	1/100	31	1350

Abbreviation: Cat., catalyst.

Conditions: 30 min at 20 °C, ethylene pressure = 5 atm, in toluene (total volume = 60 ml).

polymerization behavior. Control experiments for the reaction of **56** and 1 equiv of AlMe₃ at -20 °C revealed that the carbon atom bound to tantalum in **56** was transmetalated to aluminum to form the catalytically active tantalum-enolate species **57**, although **57** was decomposed at room temperature to give the catalytically inactive dimethyl complex **58** (Scheme 9).

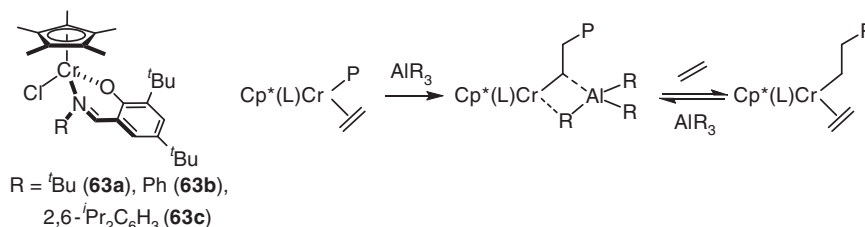
HALF-METALLOCENE GROUP 6 METAL COMPLEXES WITH ANIONIC CHELATING LIGANDS

Chromium-based catalyst systems have attracted considerable attention for their widespread commercial use in heterogeneous ethylene polymerization catalysis using CrO₃ on silica (Phillips catalyst)⁹⁰ and Cp₂Cr on silica (Union Carbide catalyst).^{91,92} Several half-chromocene complexes bearing neutral or monoanionic ligands as models for such heterogeneous catalysts have been developed.^{93–102} Some cationic alkylchromium complexes were reported by Theopold *et al.*^{103,104} as homogeneous model complexes for chromium-based ethylene polymerization catalysts. The reaction of [(η^5 -C₅Me₅)CrR¹]₂(μ -Cl)₂ (**59**, R¹ = Me, Et) with TlPF₆ in the presence of Lewis bases afforded [(η^5 -C₅Me₅)CrR¹(L)][PF₆] (**60**, R¹ = Me, Et; L = py, 3,5-lutidine, 2,2'-bipyridyl, PMe₃, 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(dimethylphosphino)methane (dmpe); Scheme 10). When the dimeric methylchromium complex was used as the starting material, the resulting cationic methylchromium complex **61** with two coordinating THF molecules was isolated and structurally characterized. Complex **61** exhibited catalytic ethylene polymerization activity, and the resulting PEs had rather narrow molecular weight distributions ($M_w/M_n = 1.41$ – 4.60) and little branching, suggesting that **61** was a single-site catalyst.

The acetylacetonato derivatives, (η^5 -C₅R₅)Cr(acac)X (**62**, R = H, Me; X = Cl, Br), were prepared by treating (η^5 -C₅R₅)CrX₂ with

sodium acetylacetonate in THF.¹⁰⁵ Excess AlEt₃ and ClAlEt₂ (Cr/Al = 1/300) proved to be the best cocatalysts for the activation of **62**, although the catalytic activities were very low (~ 1 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹). Phenoxy-imine ligands were used for bidentate support to give (η^5 -C₅Me₅)CrCl[2,4-^tBu₂-6-(CH = NR)₆H₂O] (R = ^tBu (**63a**), Ph (**63b**), 2,6-ⁱPr₂C₆H₃ (**63c**)). The ethylene polymerization activities of these complexes similarly improved on activation with a slight excess of AlMe₃ (Table 9).^{106–108} The substituent on the nitrogen atom of the phenoxy-imine ligand significantly affected the catalytic activity: the catalytic activity of **63a** with an alkyl substituent on the imine moiety was higher than that of **63b–c** bearing aromatic rings. For all of the complexes, the catalytic activity was decreased with an increase in the amount of AlR₃, indicating that the alkyl-bridged heterobimetallic chromium–aluminum species and a mononuclear chromium complex were in equilibrium in the reaction mixture (Scheme 11). Remarkably, the type of alkyl group in trialkylaluminum also influenced the catalytic behavior: bulky R groups attenuated the polymerization rate by impeding the approach of ethylene to the chromium center.

β -Ketoiminate, β -diketiminato, hydroxyindanimine and binaphthyl-based Schiff base ligands were used as six-membered chelating ligands on half-metallocene complexes of chromium (Figure 13).^{109,110} Under an atmospheric pressure of ethylene, the activity of **64a–e** and **65** depended on the cocatalyst: adding excess MAO had no effect on ethylene polymerization activity, whereas AlEt₃ (25 equiv) activated these complexes to give PE (up to 153 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹). Similarly, the complexes **66a–e** were active for the polymerization of ethylene (up to 168 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) in combination with AlEt₃. When a binaphthyl backbone was used as a ligand motif to synthesize the dinuclear half-metallocene complexes **67a–c**, the catalytic activity for ethylene polymerization was improved compared with the mononuclear analogs.



Scheme 11 Half-metallocene chromium complexes under catalytic polymerization conditions ($\text{AlR}_3/\text{C}_2\text{H}_4$).

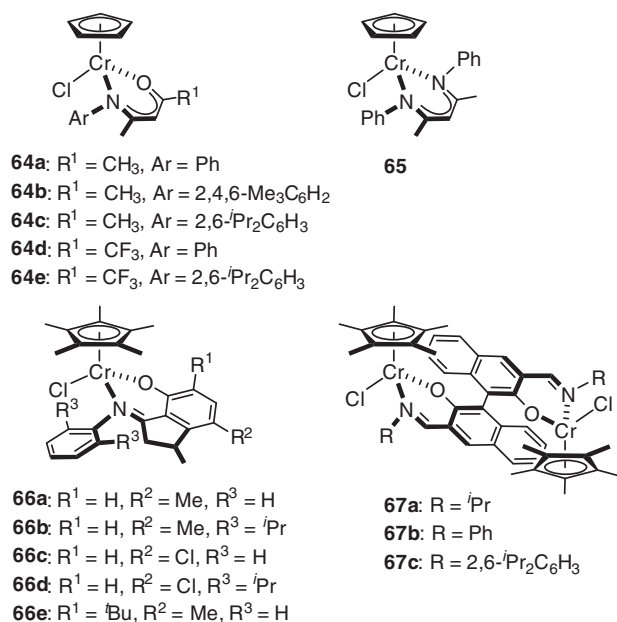
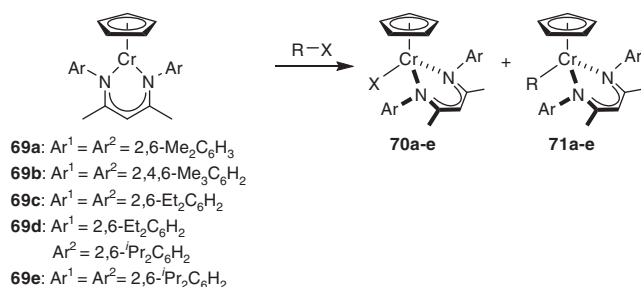


Figure 13 Half-metallocene complexes of chromium with Schiff base ligands.



Scheme 12 Controlled radical polymerization by means of half-metallocene chromium complexes.

Poli *et al.*^{111–114} reported that the 17-electron diene complexes of molybdenum ($\eta^5\text{-C}_5\text{R}_5$)Mo($\eta^4\text{-diene}$)X₂ (**68**) have very low catalytic ethylene polymerization activity (<0.02 kg-PE (mol cat)⁻¹ h⁻¹ atm⁻¹) on treatment with excess MAO, presumably due to the low polarity and high strength of the molybdenum–carbon bond. In sharp contrast to the above-mentioned coordination–insertion polymerization systems, a controlled radical polymerization reaction was achieved with half-metallocene complexes of

chromium(II) having monoanionic nacnac ligands (**69a–e**).^{115–117} The key reaction step involved the reductive cleavage of the carbon–halogen bond of the initiator to form CpCr(X)(nacnac) (**70a–e**) and CpCr(R)(nacnac) (**71a–e**), both of which formed in the reaction of **69a–e** with the generated organic and halo radicals (Scheme 12). Thus, the complexes **71a–e** dissociated with the low-oxidation state metal species **69a–e** and an organic radical, the latter of which initiated the controlled radical polymerization of styrene, acrylates and vinyl acetate.

CONCLUSION

A variety of effective and selective half-metallocene catalysts of group 4–6 metals are now available for α -olefin polymerization reactions. Therefore, *atactic* poly(α -olefin)s, poly(ethylene/ α -olefin) as well as stereoselective, stereogradient and stereoblock poly(α -olefin)s can be efficiently synthesized. The influence of the structures of the half-metallocene catalyst complexes with chelating ligands on the properties of the generated polymers is now under intense investigation to develop new classes of polymerization catalysts. The substituents on the Cp ring, the chelating ring size and the donor elements in the chelating ring are important factors for controlling the propagation step in the growing polymer chains. In addition, the fluxional behavior of various chelating ligands attached to the metal center has an important role in regulating the stereoselectivity of the polymerization. Future efforts to fine-tune the catalyst architecture may open new avenues toward the creation of unique poly(α -olefin)-based materials.

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