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Metallocene catalysts for olefin polymerization
Annual review for 1996

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Contents

Abbreviations: Cp, C_5H_5; Cp*, C_5Me_5; Cp′, generic cyclopentadienyl ligand; Ind, indenyl; H_4-Ind, tetrahydroindenyl; $Et(Ind)_2$, 1,2-ethylenebis(1-indenyl) ligand; Flu, fluorenyl; MAO, methylalumoxane.

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Abstract

This review covers research in olefin polymerization by metallocene catalysts published in 1996. While metallocenes are generally defined as metal complexes with two cyclopentadienyl rings, this review will additionally cover catalysts containing only one cyclopentadienyl ring, as well as catalysts with ligands isolobal to cyclopentadienide. Included will be certain disclosures concerning cocatalyst preparation and use. Polymer properties and uses will not be covered.

Keywords: Metallocene catalysts; Olefin polymerization; Cyclopentadienyl rings

1. Source materials

Publications to be reviewed were taken from searches of a number of online databases including Chemical Abstracts, Current Contents, Derwent World Patent Index, and US Patents Fulltext. Basic patent cases (US patents, European Patent Applications, PCT International Applications) entering the literature in 1996, either in Chemical Abstracts or Derwent's World Patent Index, are covered. Whenever a European Patent Application or PCT International Application, appearing in 1996 as a basic case, has subsequently issued as a US patent, the US patent number will be cited. When an equivalent application to a published PCT International Application in Japanese appears, usually as a European Patent Application, reference will be made to the English-language version[1].

2. Preparation of metallocene complexes

The commercial interest in exploiting metallocene complexes for olefin polymerization has led to additional efforts to prepare suitable metallocene complexes efficiently and economically. In some cases, these preparative methods are quite general and will be reviewed in this section.

Dialkylcyclopentadienylzirconium complexes are widely used in preparation of linear-low-density polyethylenes. 1,2/1,3-Alkylmethylcyclopentadienes have been prepared in good yields by reaction of methylcyclopentadiene with alkyl halides in the presence of NaOH/CaO [1]. Synthesis of dialkylcyclopentadienes can result in the formation of *endo*- and *exo*-diene isomers **1a** and **1b**. These may be efficiently separated and the *endo* isomer metalated by reaction with an excess of deprotonating agent like butyllithium, followed by reaction with $ZrCl_4$ to form the zirconocene catalyst precursor [2]. Reaction of the *exo*/*endo* diene mixture with aqueous or ethereal HCl effects the conversion to the preferred *endo* isomer [3].

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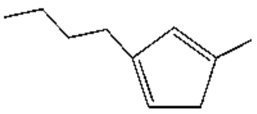
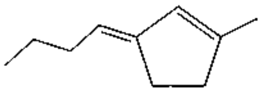
[1] The citation of a patent or patent application should not be construed as an endorsement of the validity of the claims contained therein. All opinions expressed in this review are solely those of the author.



endo

1a



exo

1b

1,2,3,4-Tetramethylcyclopentadiene is an important precursor in the preparation of $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)MCl_2$ ('constrained-geometry') catalysts. An efficient low-cost process of preparing this ligand involves pyrolysis of inexpensive isobornyl carboxylates to form a mixture of trimethylcyclopentadienes (Fig. 1). Methylation and subsequent pyrolysis affords the desired 1,2,3,4-$C_5Me_4H_2$ [4]. Heating carbonyl compounds in the presence of solid acid catalysts also produces cyclopentadienes: heating 5-methyl-4-hexen-2-one over silica/alumina at 380°C affords 1,3-dimethylcyclopentadiene [5].

Bis(cyclopentadiene) ligands bridged by C_1 units can be prepared by reaction of the cyclopentadiene (e.g. indene) with a ketone in the presence of milled KOH or NaOH [6]. Deprotonation and reaction with R'_3ECl ($E = Si$, Ge, Sn) affords $R_2C(Cp'ER_3)_2$ compounds which can be reacted with $ZrCl_4$ to give the *ansa* zirconocene (Fig. 2) [7].

A three-step method has been used to prepare silane-bridged ligands with different cyclopentadiene groups; for example, reaction of lithium 2-methylindenide with $Me_2Si(OEt)Cl$ followed by reaction with acetyl chloride and substitution by lithium cyclopentadienide affords the bridged ligand set $(C_5H_6)SiMe_2(2\text{-}MeC_9H_6)$ [8]. An active catalyst can be prepared in situ by reacting zirconium complexes with cyclopentadiene or indene in the presence of a boron or aluminum hydride,

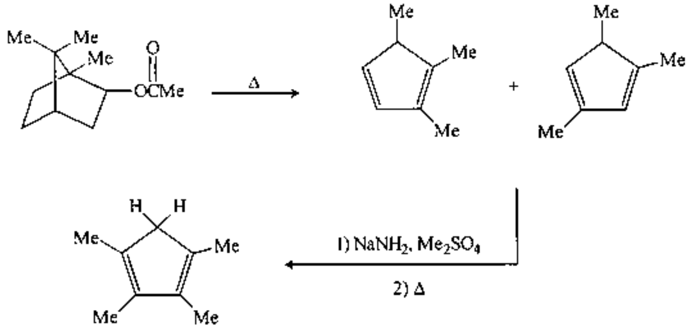


Fig. 1. Synthesis of 1,2,3,4,-tetramethylcyclopentadiene.

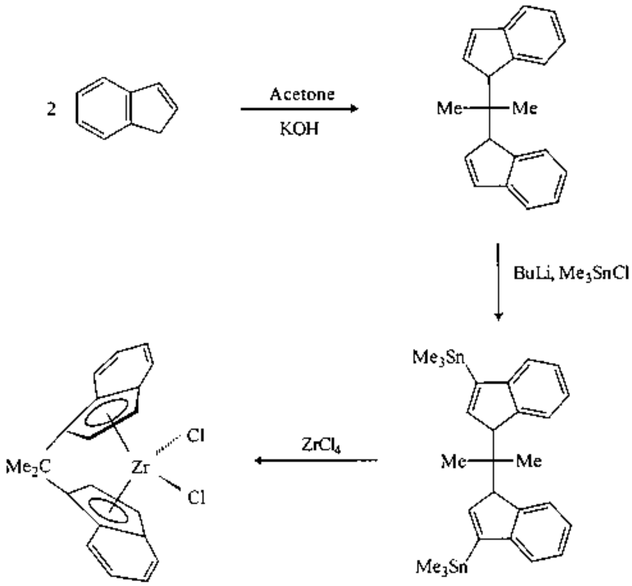


Fig. 2. Synthesis of isopropylidene bridged metallocenes.

followed by reaction with methylalumoxane (MAO) and an ionic non-aluminum activator (Fig. 3) [9].

Metallocene complexes suitable for isospecific olefin polymerization rely heavily on bridged substituted bis(cyclopentadienyl) compounds. Preparations of these compounds frequently lead to the formation of equal amounts of a racemic mixture of chiral C_2 isomers along with the undesirable achiral *meso* diastereomer, which is aspecific in α-olefin polymerization. Thus, a high yield route to the desirable *rac* isomer with minimal formation of the *meso* isomer is desirable.

Exposure to light has been used to interconvert *meso* isomers of bridged metallocene complexes like $Et(H_4\text{-}Ind)_2TiCl_2$ to *rac* isomers, but the procedure is not general: while more *rac* isomer is formed from complexes like $Et(Ind)_2ZrCl_2$, highly substituted zirconocene complexes like $Me_2Si(2\text{-}Me\text{-}4,6\text{-}i\text{-}PrInd)_2ZrCl_2$ vastly favor the *meso* isomer when irradiated [10].

Jensen has reported an improved synthesis of *rac*-$Et(Ind)_2ZrCl_2$ by simultaneous addition of the $[Li]_2[Et(Ind)_2]$ and $ZrCl_4$ in THF. Extraction of the product with CH_2Cl_2 and precipitation with pentane afforded the desired product in 66% yield [11]. Addition of TMEDA to $ZrCl_4$ before adding the dilithium salt of *ansa*-bis(indenyl) dianions has also been claimed to result in almost exclusive formation of the

$$ZrX_4 + Cp'H + \text{Activator 1} \xrightarrow[\text{[Ct][A]}]{\text{MAO}} \text{Active Metallocene Catalyst}$$

X = Cl, O-n-Pr, CH_2Ph
Cp'H = C_5H_6, C_9H_8
Activator 1 = Catecholborane, $Al(i\text{-}Bu)_2H$
[Ct][A] = $[Cp_2Fe][B(C_6F_5)_4]$, $[Ph_3C][(C_2B_9H_{11})_2Co]$

Fig. 3. Synthesis of metallocene catalysts form $ZrCl_4$ and cyclopentadienes.

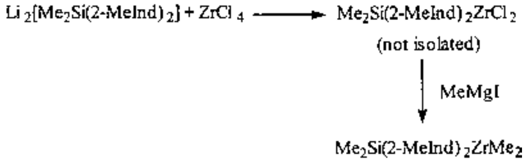


Fig. 4. Synthesis of *ansa* metallocene dimethyl complexes.

racemic product [12]. A third method of obtaining *rac ansa*-metallocenes free of *meso* isomer is a one-step preparation in which the unisolated metallocene dichloride, formed from the dilithium salt and metal chloride, is reacted with an alkylating agent like MeMgI (Fig. 4) [13].

Magnesium salts of chiral ligand dianions can be combined with Group 4 bis(diketonates) to afford the *rac* metallocenes in much higher yield (80–90%) than is possible when the alkali metal dianion is allowed to react with MCl_4 (20–40%) (Fig. 5) [14].

Jordan has found that the reaction of 1,2-bis(indenyl)ethane with $Zr(NMe_2)_4$ leads to *rac*-$Et(Ind)_2Zr(NMe_2)_2$ in a 13:1 excess over the *meso* isomer (Fig. 6) [15]. This can be converted to the dichloride derivative using $[HNMe_2][Cl]$ or Me_3SiCl. The extent to which the *rac* isomer will predominate over the *meso* is dependent on the ligand, the metal, and the leaving group (Table 1) [16]. Removal of $HNMe_2$, which catalyzes the *rac–meso* isomerization, favors formation of the *rac* isomer. The bias toward the formation of the *meso*-$Me_2Si(t\text{-}BuCp)_2Zr(NMe_2)_2$ diastereomer has been attributed to deformations in the ligand framework which can accomodate the *t*-Bu groups and the amide ligands more comfortably in the *meso* conformation.

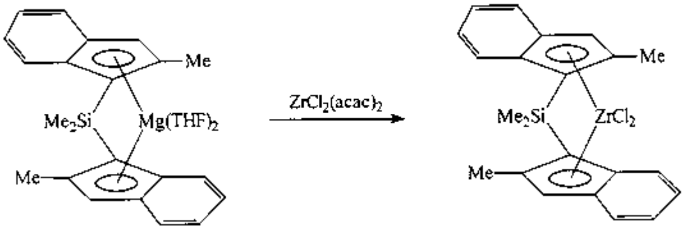


Fig. 5. Synthesis of $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ from magnesium dianion.

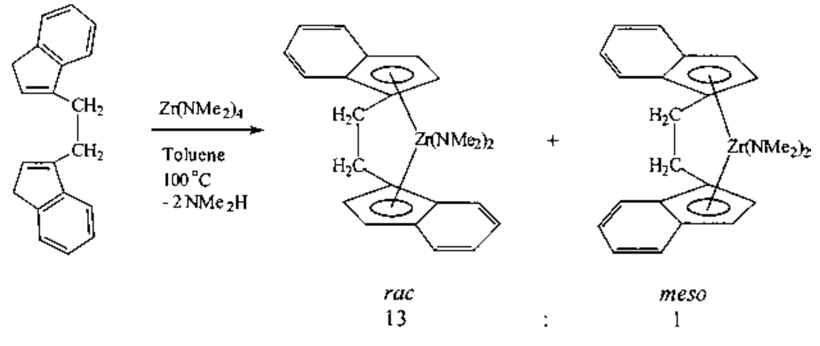


Fig. 6. Synthesis of $Et(Ind)_2Zr(NMe_2)_2$ from $Zr(NMe_2)_4$.

Table 1
Synthesis of $A(Cp')_2MX_2$ complexes from $A(HCp')_2$ and MX_4 amides

A	Cp′	M	X	Yield (*rac*) (%)	*rac*/*meso* ratio	Ref.
1,2-C_2H_4	Indenyl	Zr	NMe_2	68	13/1	[16]
1,2-C_2H_4	Indenyl	Zr	$N(CH_2)_4$	42	6/1	[16]
1,2-C_2H_4	Indenyl	Hf	NMe_2	47	7/1	[16]
Me_2Si	Indenyl	Zr	NMe_2	65	14/1	[17]a
Me_2Si	(*t*-BuCp)	Zr	NMe_2	38 (*meso*)	1/2	[17]b
Me_2Si	(2-Me-4-*t*-BuCp)	Zr	NMe_2	52	2.5/1	[17]b
Me_2Si	(2-Me-4-*t*-BuCp)	Zr	$N(CH_2)_4$	39	3/1	[17]b
Me_2Si	(2-Me-4-*t*-BuCp)	Zr	$N(CH_2)_5$	7	>20/1	[17]b

Depending on the bulk of the ligand, elimination of only one equivalent of $HNMe_2$ may take place. The reaction of $Zr(NMe_2)_4$ with $(C_5H_5)CMe_2(C_9H_7)$ results in formation of the *ansa*-metallocene, but when $(C_5H_5)CMe_2(C_{13}H_9)$ is used a mono(cyclopentadienyl) complex is formed (Fig. 7) [17].

The amine-elimination reaction using $Me_2Si(NH\text{-}t\text{-}Bu)(Cp'H)$ ($Cp' = C_5H_4$ and C_5Me_4) and $M(NMe_2)_4$ (M = Ti, Zr, Hf) has been used to prepare $Me_2Si(NR)(Cp')M(NMe_2)_2$ complexes [18]. These can be converted to the dichlorides by reaction with Me_3SiCl, but HCl or $[R_3NH]Cl$ afford amine-coordinated adducts as by-products. The use of two equivalents of the neutral ligand with $M(NEt_2)_4$ (M = Zr, Hf) gives instead the bis(cyclopentadienyl) product, which functions as a catalyst in the presence of MAO (Fig. 8) [19].

Cp_2TiCl_2, $CpTiCl_3$ or their alkoxide derivatives can be reacted with the dianion $[MgCl\cdot THF][Me_2Si(N\text{-}t\text{-}Bu)(C_5Me_4)]$ to give the constrained-geometry complex $Me_2Si(N\text{-}t\text{-}Bu)(C_5Me_4)TiCl_2$ [20].

3. Ring substituents

One of the keys to the successful utilization of metallocenes in olefin polymeriza-

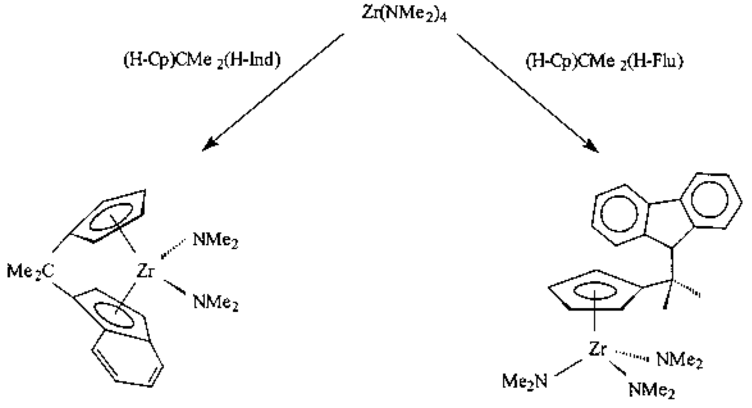


Fig. 7. Reactions of $Zr(NMe_2)_4$ with *ansa* bis(cylcopentadiene) ligands.

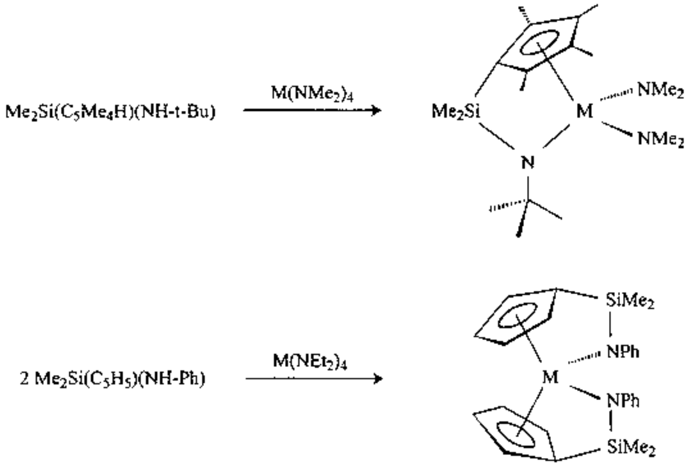


Fig. 8. Reactions of $Zr(NMe_2)_4$ with $Me_2Si(H{-}Cp')(NH{-}R)$ ligands.

tion is the ability to manipulate activity, molecular weight, comonomer incorporation, and stereopecificity by choice of cyclopentadienyl ring substituents. For the most part, up to now most ring substituents have been hydrocarbyl (alkyl or aryl) or silahydrocarbyl (e.g. $-SiMe_3$) groups. A number of novel complexes with polar groups bonded to the cyclopentadienyl ring have been discovered recently. Reaction of 2-indanone with dialkylamines affords indenyl complexes with NR_2 groups in the 2-position [21]. These can be deprotonated and the indenide salts used to prepare zirconocene and *ansa*-zirconocene procatalysts (Fig. 9). A similar methodology was used to synthesize the O-bonded *ansa*-zirconocene complex $Et(2\text{-}t\text{-}BuMe_2SiO\text{-}C_9H_5)_2ZrCl_2$ used in ethylene polymerization and isospecific propylene polymerization [22].

Metallocene complexes with somewhat more remote polar substituents have also been prepared, for example the 2-pyridyl complex **2** [23] and the 2,7-diethy-

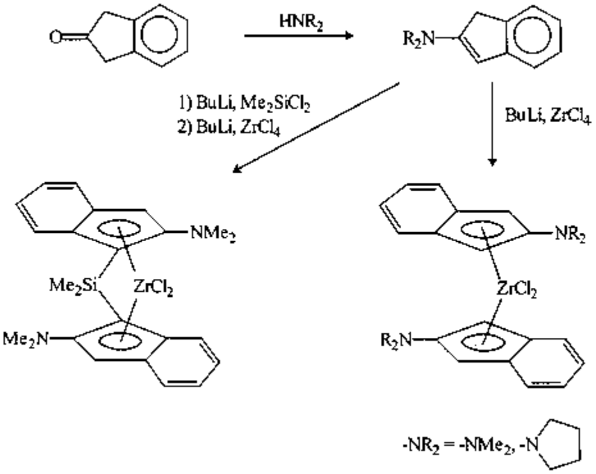
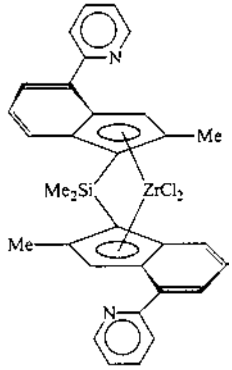


Fig. 9. Preparation of 2-amino substituted bis(indenyl) zirconium complexes.

laminofluorenyl compound **3** [24] used in stereospecific propylene polymerization. Both the metallocene complexes $(C_5H_4CH_2CH_2N(i\text{-}Pr)_2)MCl_2$ (M = Ti, Zr) and their dihydrochloride salts function as ethylene polymerization catalysts in the presence of MAO [25]; the protonated derivatives have activities as high as their amine precursors and are air- and water-stable.



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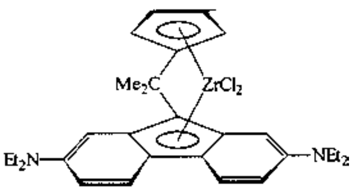
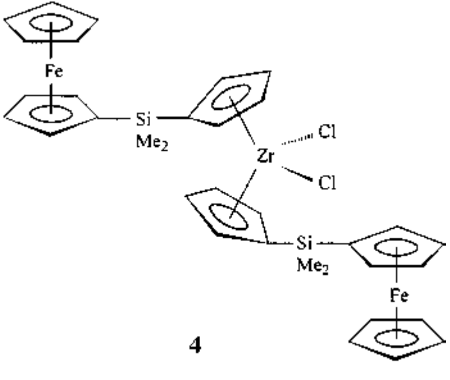


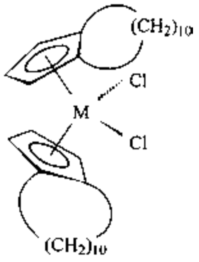
3

Ferrocenyl cyclopentadienyl groups have been reacted with $ZrCl_4$ to produce zirconocenes such as **4** with dimethylsilylferrocenyl ring substitutents. These were more active than Cp_2ZrCl_2 when cocatalyzed by MAO or $[Ct][B(C_6F_5)_4]-Al(i\text{-}Bu)_3$ ($Ct^+ = HNMe_2Ph^+$, Ph_3C^+) and terpolymerizes ethylene, propylene, and diene more efficiently than the unsubstituted zirconocene [26].



4

Annulated rings, in which two adjacent ring substituents are joined, have hitherto been largely derivatives of indenes and fluorenes. New complexes have recently been prepared with larger rings. The 12-membered ring complexes **5** (M = Ti, Zr, Hf) have been characterized by X-ray crystallography (M = Ti, Zr) [27]. The Cp rings are almost eclipsed and the rings are, surprisingly for so bulky a substituent, on the same side (*meso* arrangement). Complexes with annulated seven-membered rings (**6**) are prepared by nucleophilic attack on azulene derivatives, followed by bridging and metalation with $ZrCl_4$. These serve as catalyst for isospecific propylene polymerization [28].



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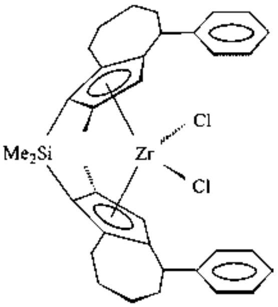

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4. Bridging groups

Interannular bridges in bis(cyclopentadienyl) metal complexes serve to fix the rings in a particular orientation and affect the performance of the catalyst by changing the ring–metal–ring angle, thereby opening the active site. 1,2-Ethylene bridges and dimethylsilyl units have been widely used as bridges, but other groups have been reported in 1996.

The tin-bridged metallocene $Me_2Sn(C_5H_4)_2Zr(NMe_2)_2$ and the binuclear complex $(Me_2N)_2Zr(C_5H_4)_2Sn(C_5H_4)_2Zr(NMe_2)_2$ were prepared by reaction of $Me_2Sn(C_5H_5)_2$ or $(C_5H_5)_4Sn$ with $Zr(NMe_2)_4$ [29]. The mononuclear tin-bridged metallocene is considerably more active than its Me_2Si-bridged counterpart in ethylene polymerization cocatalyzed by MAO (6.84 vs. 3.54 kg PE $mmol^{-1}$ Zr h^{-1}).

Hydropentalene derivatives have an annulated fulvene structure to which cy-

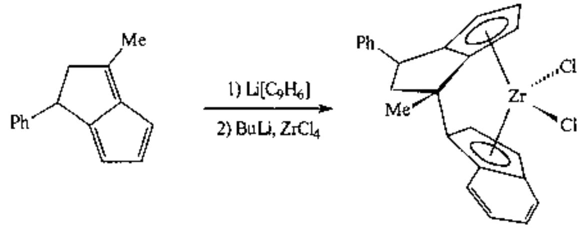
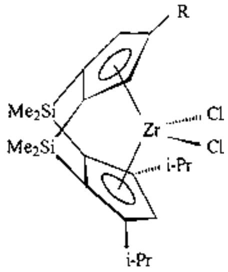


Fig. 10. Synthesis of *ansa* zirconocene form dihydropentalenes.

clopentadienides or indenes can add to form bis(cyclopentadienyl) metal derivatives in which the two rings are bridged by a fused-ring unit (Fig. 10) [30]. These bridged metallocenes have been used in the copolymerization of ethylene with cyclic olefins.

An unusual cationic Me_2P^+ group was used by investigators at BASF to link two 2-methyl-4-*t*-BuCp rings (Fig. 11) [31]. This complex was used to polymerize propylene when activated by MAO. In contrast, the neutral phosphine bridged precursor MeP(2-Me-4-*t*-BuCp)$_2$ZrCl$_2$ showed no activity under similar conditions.

The double bridged complexes **7**–**10** are stereospecific catalysts for the polymerization of propylene. The bis(dimethylsilyl)-bridged complex **7** functions as a syndiospecific catalyst as it posseses C_s-symmetry, cyclopentadienyl groups of different size and an open region between the isopropyl substituents to accomodate a downward-directed methyl group on the incoming propylene monomer [32]. The silaspiro metallocene **8**, which posseses C_2-symmetry, polymerizes propylene to isotactic polypropylene [33] as does the bis(1,2-ethylene)-bridged bis(indenyl) zirconocene **9** [34]. The C_s-symmetric complex **10** ($M = Ti$, Zr) displays very low activity and affords almost completely atactic PP [35].



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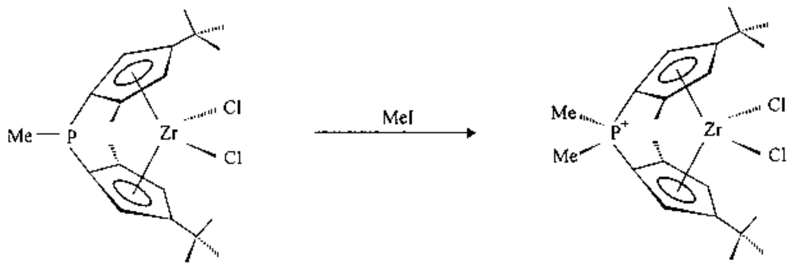
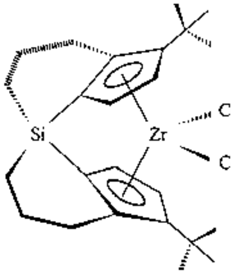


Fig. 11. Quaternization of MeP(2-Me-4-*t*-Bu)$_2$ZrCl$_2$.



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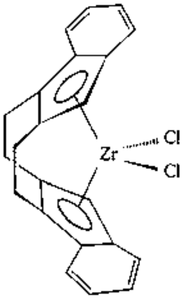

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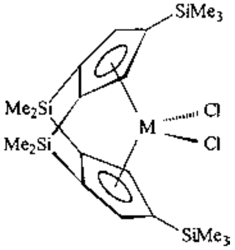

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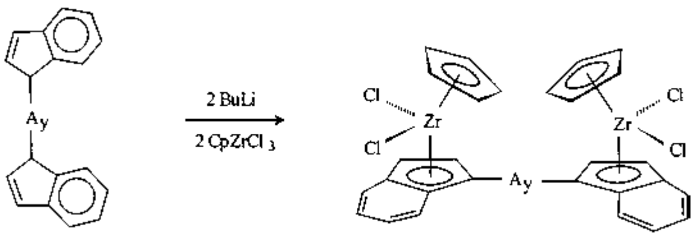
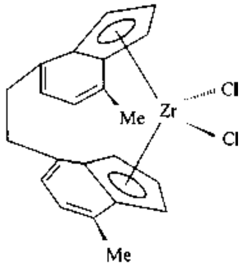
Three contemporaneous publications detailed the preparation and polymerization behavior of a new class of *ansa* metallocenes [36]. These are bridged bis(indenyl) complexes, but the bridge connects the six-membered rings, not the five-membered rings as in conventional Et(Ind)$_2$ZrCl$_2$ or Me$_2$Si(Ind)$_2$ZrCl$_2$. Compound **11**, which bears no substituents on the five-membered ring, is aspecific with respect to propylene polymerization, while *pseudorac*-**12** affords isotactic polypropylene.



y = 0; y = 1, A = Me $_2$SiCH $_2$CH $_2$SiMe $_2$

Fig. 12. Synthesis of binuclear zirconocenes form bridged bis(indenes).



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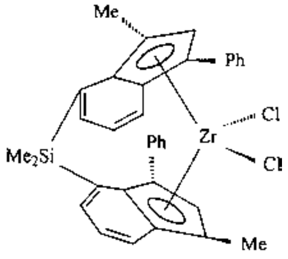

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5. Binuclear complexes

Metallocene catalyst systems containing more than one metal center have the potential to create polymers controlled breadth of molecular weight and comonomer distribution through mixtures of metal centers, different ligand environments, or both. It is well known that separate metallocene compounds will produce polymers with broadened polydispersities, but catalysts with two polymerizing centers within the same molecule are still relatively rare.

Investigators at Tosoh have dimerized the indenide anion with $CuCl_2$; the biindene can be deprotonated and reacted with $CpZrCl_3$ to give a binuclear metallocene complex. This compound polymerizes ethylene with MAO or $Al(i\text{-}Bu)_3$–$[HNMe_2Ph][B(C_6F_5)_4]$ [37]. Similarly, the reaction of $CpZrCl_3$ with the dian-

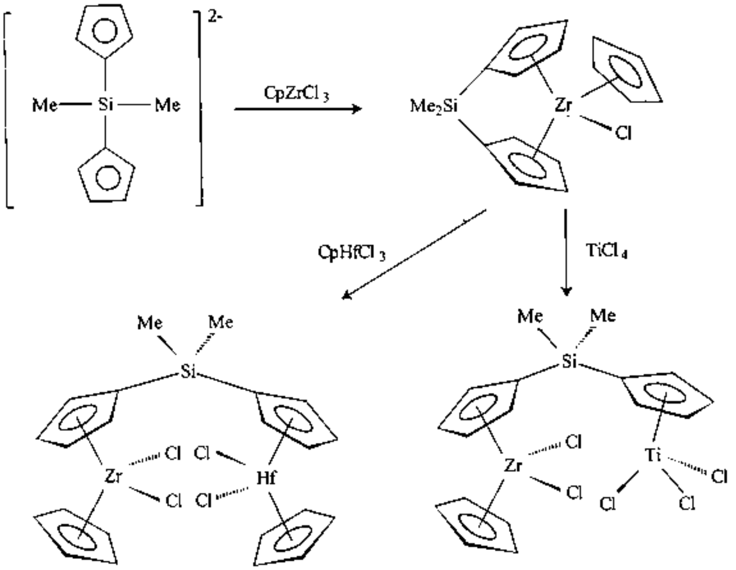


Fig. 13. Synthesis of binuclear complexes from $Me_2Si(Cp)_2Zr(Cp)Cl$.

ion $[(Ind)Me_2SiCH_2CH_2SiMe_2(Ind)]^{2-}$ gives a binuclear procatalyst with a tetramethyldisilabutane bridge between the two metallocene moieties (Fig. 12) [38] and siloxane-bridged dinuclear complexes have been synthesized from $[Cp{-}Me_2Si{-}O{-}SiMe_2{-}O{-}Me_2Si{-}Cp]^{2-}$ and $TiCl_4$ [39] or $(Ind)ZrCl_3$ [40].

Green and co-workers have disclosed a method of making binuclear metallocene complexes in which both the metal center and ligand environments can differ [41].

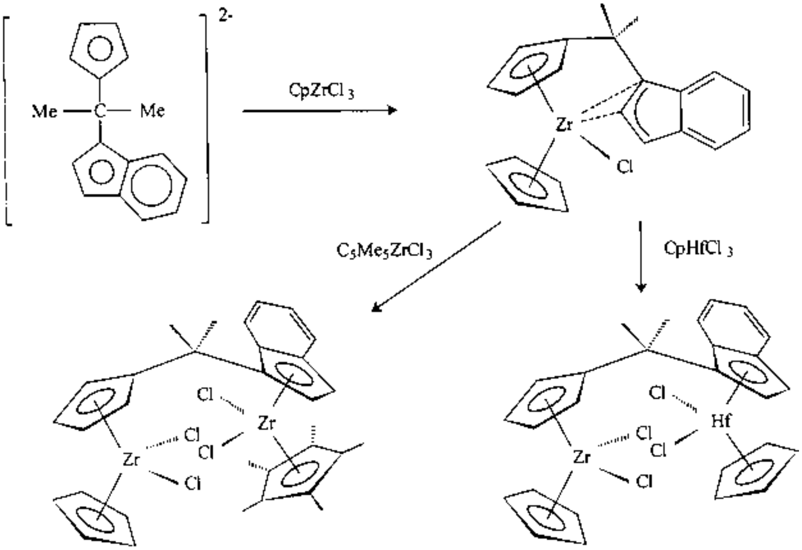


Fig. 14. Synthesis of binuclear complexes from $(\eta^5\text{-Cp})Zr(\eta^5\text{-Cp-Me}_2C\text{-}\eta^3\text{-Ind})Cl$.

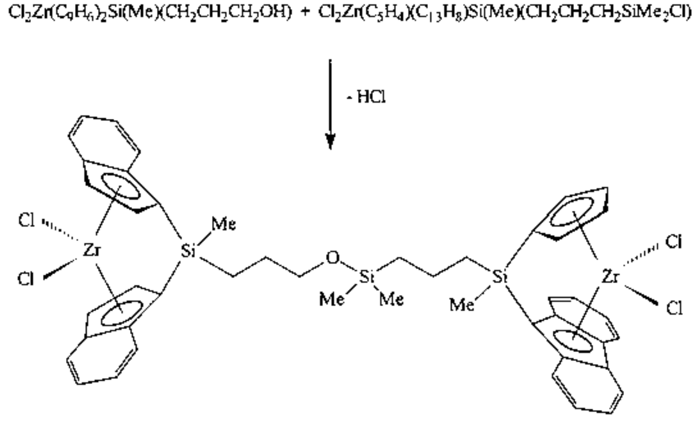


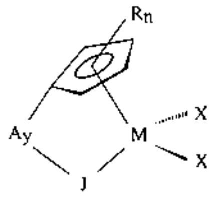
Fig. 15. Synthesis of binuclear complexes with isospecific and syndiospecific sites.

Reaction of a bridged bis(cyclopentadienyl) dianion with one equivalent of $CpMCl_3$ forms a complex in which three cyclopentadienyl rings are bonded (either η^5 or η^3) to the metal atom. Reaction with a second equivalent of metal chloride ($Cp'MCl_3$ or MCl_4) gives a binuclear complex (Figs. 13 and 14).

Specially bridged metallocenes can also be coupled to form polynuclear metal complexes. Elimination of HCl from a mixture of (3-hydroxypropyl)methylsilylbis(indenyl)zirconium dichloride and (3-chlorodimethylsilylpropyl)methylsilyl(cyclopentadienyl)(fluorenyl)zirconium dichloride affords a binuclear complex with both isospecific and syndiospecific catalyst sites (Fig. 15) [42].

6. Mono(cyclopentadienyl) complexes

Until fairly recently, mono(cyclopentadienyl) metal catalysts were far less studied than their bis(cyclopentadienyl)-based analogues. With the discovery of the utility of $Cp'TiX_3$ complexes as procatalysts for syndiospecific styrene polymerization and the commercial development of the bridged cyclopentadienyl–amide (constrained-geometry) compounds for ethylene polymerization and copolymerization, structural variations in catalysts comprising only one Cp ring have grown in number. A general structure for bridged and unbridged complexes (**13**) is shown.

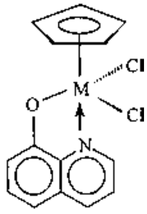


A = Bridging group, J = X, OR, NR'_2 (y = 0); J = NR' (y = 1)

13

Novel mono(cyclopentadienyl)amide compounds reported in 1996 include those in which J = adamantylamide, which has been claimed to give polymers with higher molecular weights and excellent comonomer incorporation [43], and $Me_2Si(N\text{-}t\text{-}Bu)(R{-}C_9H_5)TiCl_2$ complexes (R = H, 3-Me, 3-CH_2SiMe_3) [44].

Unbridged mono(cyclopentadienyl) complexes of the general formula $Cp'MX_2Y$ wherein Y is a heterogroup include $Cp^*TiCl_2(NR_2)$ (R = Et, $SiMe_3$) [45] and complexes in which one of the chlorides has been replaced by a hydroxyquinolyl group (**14**) [46].



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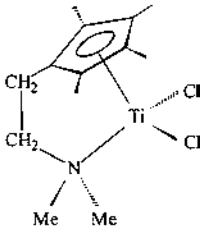
Ti(III) complexes have never figured prominently in metallocene polymerization catalysis; received wisdom says trivalent titanium complexes have much lower activities relative to their d^0 counterparts. The family of mono(cyclopentadienyl)amine catalysts developed by DSM may revise this thinking. These 'Lovacat' (for *Lo*w *Va*lent *Cat*alysts) complexes (**15**) exhibit high activity and excellent high-temperature performance when activated by MAO, or, with methylated derivatives, $[HNMe_2Ph][B(C_6F_5)_4]$ [47].



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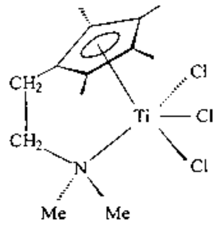
A similar complex (**16**) with a Ti(IV) center has been prepared by Chien and Rausch [48]. The catalyst resulting from activation by MAO or $Al(i\text{-}Bu)_3$–$[Ph_3C][B(C_6F_5)_4]$ has diminished activity in styrene polymerization relative to Cp^*TiCl_3, but rather higher activity in propylene polymerizations. Reaction of $(C_5Me_4CH_2CH_2Ph)TiMe_3$ with $[Ph_3C][B(C_6F_5)_4]$ affords a polymerization-active catalyst [49]. Spectroscopic and polymerization data indicate that the η^6-coordinated adduct is present (**17**). In contrast, the zirconium cation **18**, generated from $Me_2Si(\eta^5{:}\eta^2\text{-}C_5H_3CH_2CH_2NMe_2)(N\text{-}t\text{-}Bu)ZrMe_2$ and MAO, is inactive for propylene polymerization because of the dimethylamino coordination occupying the active polymerizing site [50].



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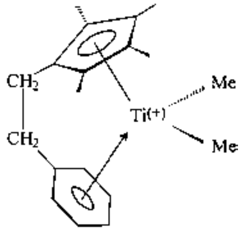

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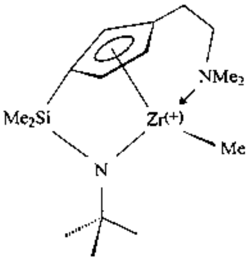

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Reaction of fulvenes with lithium diphenylphosphinomethylide forms the 1-dimethylphosphino-2-cyclopentadienide anion, which is allowed to react with $ZrCl_4$ to give a mono(cyclopentadienyl)zirconium trichloride with a chelating dimethylphosphino group (Fig. 16) [51]. As polymerization catalysts, these half-zirconocene complexes are surprisingly ethylene selective, despite their sterically unconstrained active site.

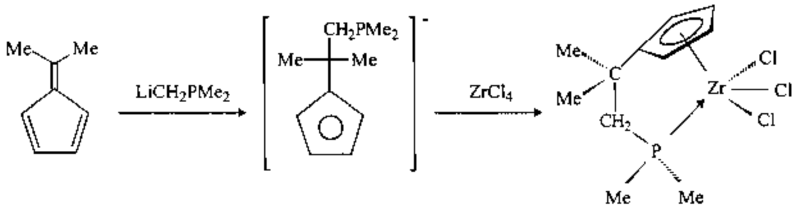
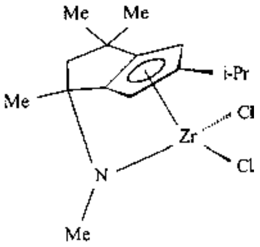


Fig. 16. Mono(cyclopentadienyl) zirconium complex from dimethylfulvene.

An unusual new class of bridged mono(cyclopentadienyl) metallocene procatalysts has the bridging group bonded to the annulated ring instead of the ring carbons of the cyclopentadienyl group. The 2,2,4-trimethyl-4-methylaminotetrahydropentalene compound **19** [52] and the 4-phenoxyindenyl complex **20** [53] are representatives of these procatalysts.



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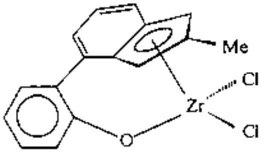

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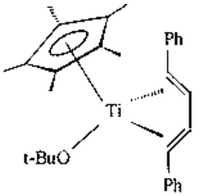
7. Non-cyclopentadienyl ligands

The nature of the X groups in Cp'_2MX_2 and $Cp'MX_3$ procatalysts and the structures of the catalysts derived therefrom have been of interest to investigators and some results were reported in 1996.

Researchers at Dow have made an intensive study of diene complexes of the Group 4 metallocenes as procatalysts for olefin polymerization, with the publication of numerous patents and patent applications. Representative examples of mono- and bis(cyclopentadienyl) metallocene complexes prepared with diene ligands are shown (**21**–**24**). These may be allowed to react with $[R_3NH][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ to form active catalysts for olefin polymerization and copolymerization [54]. With the neutral activator, an equilibrium of zwitterionic products (between η^1-butenyl and η^3-allyl) are formed.



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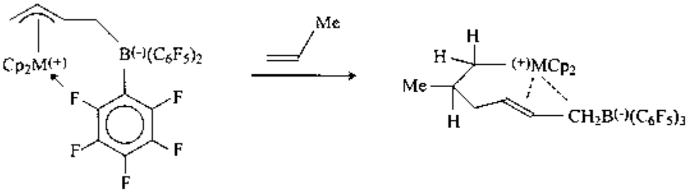
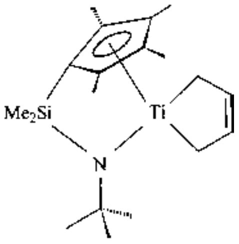


Fig. 17. Propylene reaction with a zirconocene zwitterion.



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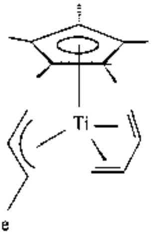

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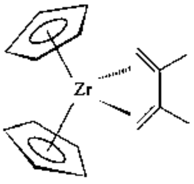

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The zwitterionic product formed from $Cp_2Zr(\eta^4\text{-}C_4H_6)$ and $B(C_6F_5)_3$ has proved useful in determining structures in the initial steps of polymerization. One equivalent of propene inserts to form only one of the four possible stereo- and regioproducts (Fig. 17) [55]. A *trans*-C=C bond is also indicated in the ^{13}C- and ^{1}H-NMR spectra of the insertion adduct.

The zirconacyclopentadiene complex reacts with $B(C_6F_5)_3$ to afford another zwitterionic product in which the Cp ring undergoes electrophilic aromatic substitution by the boron activator with transfer of the ring proton to the butadienyl moiety (Fig. 18) [56].

The reaction of CO_2 with $(C_9H_8)Zr(NMe_2)_3$ results in the formation of the tris(dimethylcarbamate)complex, which polymerizes olefins when activated by

MAO (Fig. 19) [57]. The fate of the dimethylcarbamate ligands was not disclosed. When 1,2-Et(Ind)$_2$Zr(NMe$_2$)$_2$ is reacted with AlMe$_3$, the zirconocene dimethyl complex is formed quantitatively along with Al$_2$Me$_{6-n}$(NMe$_2$)$_n$. Subsequent reaction with [Ph$_3$C][B(C$_6$F$_5$)$_4$] forms the zirconcene cation, which polymerized propylene stereospecifically [58].

'Double-bound' metallocenes, in which one of the ring substituents is also σ-bonded to the metal, can be prepared by reaction of metallocenes with ω-unsaturated alkenyl substituents with hydride reagents (Fig. 20) [59]. These function as ethylene polymerization catalysts when activated by MAO.

(C$_5$H$_5$)$_2$Zr(P(SiMe$_3$)$_2$)$_2$ reacts with Ni(CO)$_4$ or Mo(CO)$_6$ to form the early/late bimetallic complex (C$_5$H$_5$)$_2$Zr(μ-P(SiMe$_3$)$_2$)$_2$M(CO)$_n$ ($M = $ Ni, $n = 2$; $M = $ Mo, $n = 4$) [60]. When reacted with MAO, catalysts active in ethylene polymerization are obtained. Based on the IR spectra of the catalyst adduct, the carbonyl groups are interacting with an electrophilic center, but the nature of the active species is not known.

Polystyryl anion macromers, produced from styrene and sec-butyllithium can be reacted with Cp*TiCl$_3$ to produce Cp*Ti(PS)$_3$ [61]. Subsequent reaction with B(C$_6$F$_5$)$_3$ generates an active catalyst for syndiospecific styrene polymerization [62].

8. Ligands isolobal to cyclopentadienide

As the compounds based on the bis(cyclopentadienyl) framework increase,

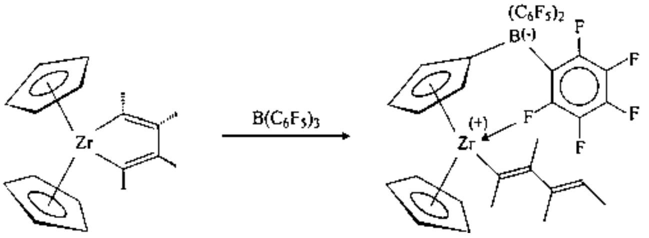


Fig. 18. Electrophilic ring substitution by B(C$_6$F$_5$)$_3$.

$$(C_9H_7)M(NMe_2)_3 + 3\,CO_2 \longrightarrow (C_9H_7)M(O_2CNMe_2)$$

Fig. 19. Reaction of (Ind)Zr(NMe$_2$)$_3$ with CO$_2$.

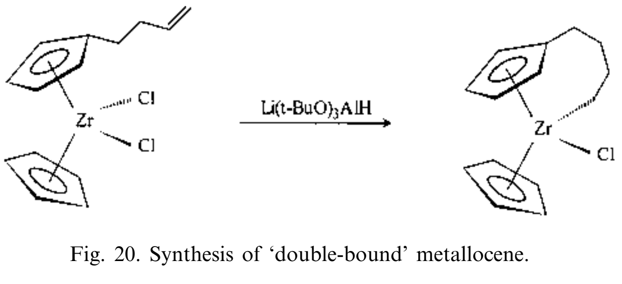
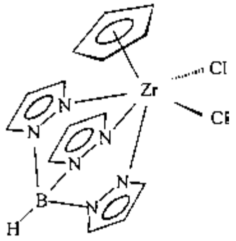


Fig. 20. Synthesis of 'double-bound' metallocene.

structures become more elaborate, and the intellectual property picture becomes cloudier, a number of investigators are turning to non-cyclopentadienyl ligands as a means of producing unique catalyst systems which retain their 'single-site' character. The year 1996 saw reports of several unique catalyst systems bearing ligands isolobal to cyclopentadienide.

Tris(pyrazolyl)borates salts were allowed to react with $Cp'MCl_3$ to give the $(HB(Pz)_3)Cp'MCl_2$ complexes **25**. These and their dimethyl derivatives polymerized ethylene and copolymerized ethylene and 1-hexene in the presence of MAO or $[HNMe_2Ph][B(C_6F_5)_4]$ [63]. Azaaromatic anions such as carbazolyl and tetramethylpyrrolyl similarly formed $Cp'M(L)Cl_2$ complexes **26** with $Cp'MCl_3$ and were also polymerization active when cocatalyzed by MAO [64].



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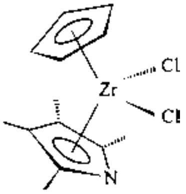

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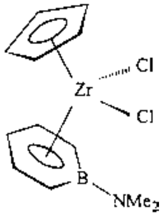
Borabenzene anions are isolobal with the cyclopentadienide anion and have been employed as ligands for single-site catalysts. Reaction of $Li(TMEDA)(C_5H_5BNMe_2)$ with $CpZrCl_3$ affords the borabenzene complex **27**, which exhibits high activity as an ethylene polymerization catalyst when contacted with MAO [65]. The bis(azaborolinyl) complex **28** is similarly polymerization active [66].



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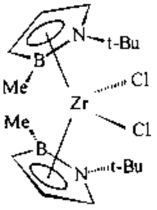

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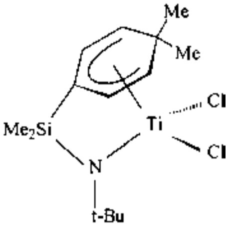
The unusual bridged cyclohexadienyl–amide complex **29**, prepared by investigators at Dow Chemical, is an isolobal analogue of the well-known constrained-geometry cyclopentadienyl–amide complexes. Anions derived from substituted acyclic dienes and 1,2-dihydronaphthalene were also used as ligands [67]. Formally Ti(II) complexes like the pentamethylcyclopentadienyl dimethylpentadienyl complex **30** polymerize styrene syndiospecifically, though the pentadienyl group may not function as an ancillary ligand in these catalysts [68].



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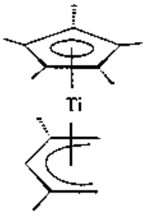

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9. Metallocene catalysts of the Group 5 and 6 metals

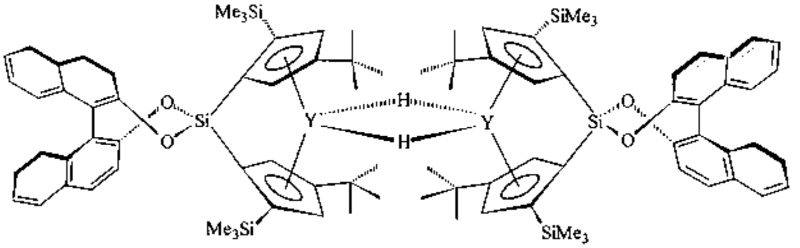
The constrained-geometry ligand $Li_2[Me_2Si(N\text{-}t\text{-}Bu)(C_5Me_4)]$ has been allowed to react with $CrCl_3(THF)_3$ to give $Me_2Si(N\text{-}t\text{-}Bu)(C_5Me_4)CrCl(THF)$. Reaction with $LiCH_2SiMe_3$ affords the Cr(III) alkyl complex $Me_2Si(N\text{-}t\text{-}Bu)(C_5Me_4)CrCH_2SiMe_3$, which functions as an ethylene polymerization catalyst without a cocatalyst [69]. Propylene is dimerized to 2-methyl-1-pentene, but higher α-olefins are unreactive toward this complex. The anionic chromium complex $[Li][Cp^*Cr(CH_2Ph)_3]$ polymerizes ethylene when supported on aluminophosphates to give polyethylene with broad molecular weight distributions. There is a marked sensitivity of catalyst performance in the presence of hydrogen or α-olefin comonomers. The unsupported catalyst is considerably less active [70].

1,3-Dienes are polymerized to predominantly *cis*-1,4 polymers by $Cp'VCl_2(PEt_3)_2$ ($Cp' = Cp$, MeCp) or Cp_2VCl when cocatalyzed by MAO, while the known $V(acac)_3$–MAO catalyst affords *trans*-1,4 polymers exclusively [71]. The mono(cyclopentadienyl) complex is considerably more active than the bis(cyclopentadienyl) compound.

10. Metallocene catalysts of the Group 3 metals and lanthanides

As neutral 14-electron three-coordinate complexes, metallocenes of the Group 3 metals and lanthanides attract interest because they can function as polymerization catalysts without activation by a cocatalyst. This makes them ideal as probes of the fundamental polymerization processes.

Ansa yttrocenes in which the 2-$SiMe_3$-4-*t*-BuCp rings are linked by binaphtholatosilylene groups allow the formation of enantiomerically pure metallocenes. The hydride dimer **31**, produced by hydrogenolysis of the $-CH(SiMe_3)_2$ derivative, polymerized 1-pentene to highly isotactic polymer (mmmm pentads > 95%) [72]. This catalyst has also been used to probe facial selectivity in α-olefin polymerizations. Using optically active (*R*)-1,1,3,4,4,5,5-octadeutero-1-pentene and following the product formation by ^{2}D-NMR, it was found that in the deuterodimerization the insertion of the olefin in the Y–H bond (**32a**) had only a slight facial preference (ee = 34%), but insertion of a second monomer into the Y–*n*-pentyl bond (**32b**) occurred with > 40:1 enantioselectivity [73].



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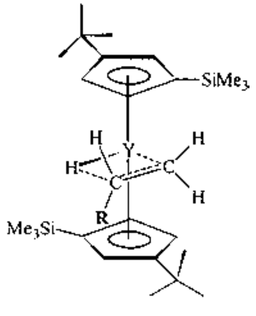
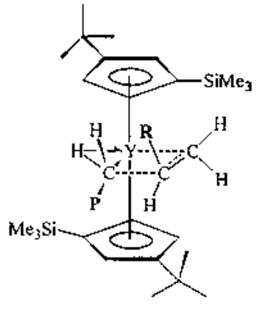


Slightly Favored

32a



Strongly Favored

32b

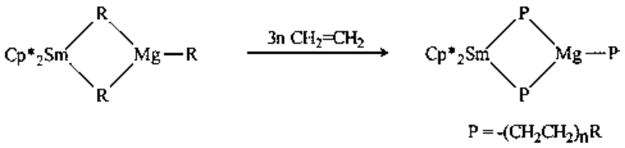


Fig. 21. Ethylene insertion into Cp$^*_2$Sm(η-R)$_2$MgR.

In the presence of BuEtMg, Cp$^*_2$Sm(μ-Cl)$_2$Li(OEt$_2$)$_2$ converts ethylene to low molecular weight waxes ($M_W = 400–3100$) with very low polydispersities ($M_W/M_N = 1.2–1.5$) even at 80°C [74]. The polymerizing species undergoes alkyl exchange with the magnesium cocatalyst such that $\{R(CH_2CH_2)_n\}_2Mg$ complexes are formed (Fig. 21). The molecular weight distribution of the polymer broadens when the $\{R(CH_2CH_2)_n\}_2Mg$ species precipitates from solution and a conventional Cp$^*_2$SmR polymerization catalyst is formed.

The neutral samarium complexes *rac*-Me$_2$Si(2-SiMe$_3$-4-*t*-BuCp)$_2$Sm(THF)$_2$, *meso*-Me$_2$Si(Me$_2$SiOSiMe$_2$)(3-*t*-BuCp)$_2$Sm(THF)$_2$, and the C_1-symmetric complex Me$_2$Si(2,4-(SiMe$_3$)$_2$Cp)(3,4-(SiMe$_3$)$_2$Cp)Sm(THF)$_2$ polymerize ethylene to linear polyethylene with molecular weights as high as 10^6 and with narrow molecular weight distributions [75]. The *rac* complex also polymerizes α-olefins to isotactic polymers. (*t*-Bu$_2$Cp)$_2$Yb(THF) polymerizes styrene, but it is not clear whether this is coordination polymerization or radical initiation [76].

The neodymium complexes Li[(C$_5$R$_5$)Nd(C$_3$H$_5$)$_3$]$\cdot$L (R = H, Me; L = dioxane, DME) polymerize butadiene to polybutadiene. The active species is generated by loss of allyllithium from the complex, a process which can be modulated by Lewis acids like BEt$_3$ or AlEt$_2$Cl or by donor molecules such as THF or dipipyridylethane (Fig. 22) [77].

$$Li[(C_5Me_5)Nd(C_3H_5)_3] \rightleftharpoons (C_5Me_5)Nd(C_3H_5)_2 + LiC_3H_5$$

Fig. 22. Dissociation of Li(C$_3$H$_5$) from Li[Cp*Nd(C$_3$H$_5$)$_3$].

Table 2
Effect of Me/Al ratio on polymerization activity

Me/Al ratio	$AlMe_3$ (mol%)	Average M_W	Activity (kg PE g^{-1} Zr h^{-1} atm^{-1})
1.63	29.0	420	330
1.55	27.5	590	719
1.50	25.5	805	860

Polymerization catalysts of the Group 3 metals and lanthanides are frequently bis(cyclopentadienyl) complexes with sterically demanding ancillary ligands to suppress dimerization. A series of mono(cyclopentadienyl) analogues $(HB(3,5\text{-}Me_2Pz)_3)YR_2(THF)$ ($R = Ph$, Me, CMe_3, CH_2SiMe_3) polymerize ethylene without a cocatalyst despite a relatively open active site [78]. Dissociation of THF from the metal center is part of the polymerization process; the complexes are inactive in THF solution.

11. Activator compounds

For the most part, metallocene catalysts are comprised of two parts, the metal complex and an activating cocatalyst. This review will include some research carried out on new activating species for metallocene and other single-site olefin polymerization catalysts.

Methylalumoxane (MAO), the product of the controlled reaction of trimethylaluminum and water, remains the most frequently used cocatalyst in metallocene polymerizations. It is by far a superior cocatalyst to other hydrolyzed aluminum alkyls. For example, ethylene polymerization activities by Cp_2ZrCl_2 were found to be 100 times lower when tetraisobutyldialumoxane was used as the cocatalyst rather than MAO [79]. Attempts to find substitutes continue, however: investigators at Montell have disclosed that more branched trialkylaluminums and dialkylaluminum hydrides such as tris(2,4,4-trimethylpenyl)aluminum or 2-phenylpropyl-modified diisobutylaluminum hydride, when contacted with water, are far more effective cocatalysts for metallocene complexes than is tetraisobutyldialumoxane [80].

Reddy and co-workers examined the catalytic behavior of Cp_2ZrCl_2 with MAO of varying composition [81]. As can be seen in Table 2, MAO solutions with low Me/Al ratios containing less $AlMe_3$—through hydrolysis at higher temperatures over longer periods—are more effective cocatalysts than alumoxanes from $AlMe_3$ hydrolyzed under milder conditions.

Whatever its virtues as a cocatalyst, MAO remains an ill-defined material, probably an oligomeric distribution of partially hydrolyzed $AlMe_3$ and associated with variable amounts of starting material, which have been deemed the source of fouling in supported catalysts. Post-hydrolysis treatment of MAO with emulsified water [82] or ene-ols like allyl alcohol [83] have been claimed to reduce the amount of reactor fouling when used with supported metallocene–MAO catalysts.

Treatment of MAO solutions with aluminates ($NaAlO_2$), silicates (Li_2SO_3), or carbonates (Na_2CO_3) precipitates an insoluble $AlMe_3$-free alumoxane which can be combined with metallocenes to give heterogeneous polymerization catalysts [84]. Soga and co-workers allowed MAO solutions to react with *p*-hydroquinone to precipitate a toluene-insoluble material which is ineffective by itself as a cocatalyst for $Et(Ind)_2ZrCl_2$. Addition of Al(*i*-Bu)$_3$ restores the catalytic activity. The authors have speculated that the *p*-hydroquinone/MAO product is essentially free of Al–Me groups and thus cannot methylate the metallocene dichloride. Triisobutylaluminum serves to alkylate the metallocene, which alkyl group can be abstracted by the modified MAO to generate an active catalyst [85].

Non-aluminum activators such as $B(C_6F_5)_3$ or $[Ct][B(C_6F_5)_4]$ (Ct^+ = alkyl- or hydride-abstracting cation) may obviate many of the disadvantages of MAO as an activator for metallocene catalysts. Many cations have been developed for the $[B(C_6F_5)_4]^-$ anion, most recently silylium salts, prepared by metathesis of $Li[B(C_6F_5)_4]$ with R_3SiCl [86].

The boron activators abstract an alkyl group from the metallocene dialkyl. The active catalyst can be generated by reacting the metallocene dichloride with an aluminum alkyl, followed by the boron activator. A study indicates that MAO and branched aluminum alkyls such as triisobutylaluminum are preferable alkylating agents to triethylaluminum [87].

A polymer-bound non-interfering anion was prepared by copolymerizing trimethylammonium or dimethylanilinium salts of 4-vinylphenyltris(pentaflurophenyl)borate with styrene or pentaflurophenylstyrene (Fig. 23) [88]. Reaction of this ionomeric copolymer with metallocene dimethyl complexes affords an active catalyst which polymerizes ethylene in a slurry process. No fouling of the reactor walls was observed.

Reaction of the novel activator compound $HB(C_6F_5)_2$ (prepared from $ClB(C_6F_5)_2$ and $HSnBu_3$) with $Cp_2Zr(CH_2Ph)_2$ results in the loss of toluene to give a zwitterionic product, which is active in ethylene polymerization (Fig. 24) [89].

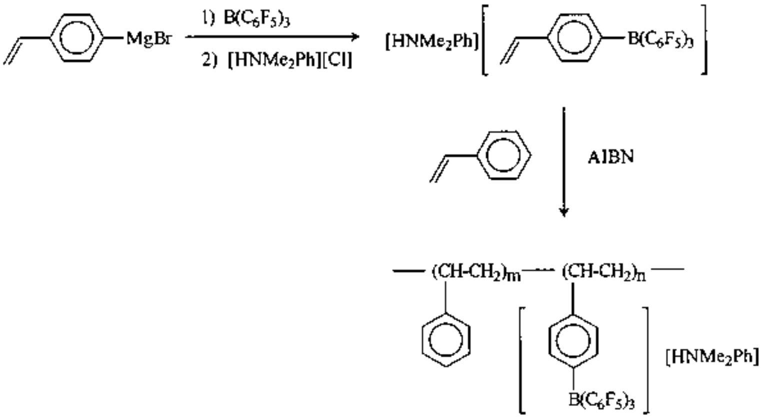


Fig. 23. Preparation of polymer-bound borate activator.

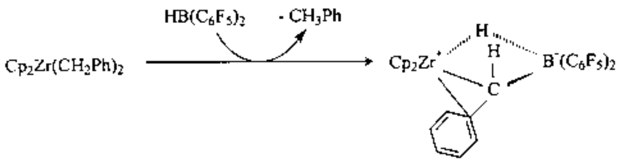
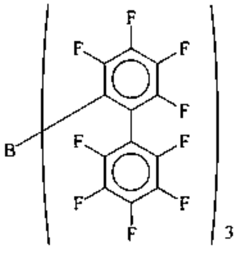


Fig. 24. Reaction of $Cp_2Zr(CH_2Ph)_2$ with $HB(C_6F_5)_3$.

Tris(pentafluorophenyl)boron is a widely used activator for coverting metallocene dihydrides and dialkyls to cationic catalysts. It has been prepared by reaction of C_6F_5MgBr (from C_6F_5Br and alkylmagnesium halides) with $BF_3 \cdot$etherate. Use of the less expensive C_6F_5Cl and *i*-PrMgBr has been found to work equally well [90]. After reaction of the Grignard reagent with $BF_3 \cdot$etherate, the magnesium salts can be precipitated with 1,4-dioxane or 1,3-dioxolane to give $(C_6F_5)_3B \cdot$etherate, which can be extracted into aromatic or aliphatic solvents to give an ether-free solution [91].

Reaction of $B(C_6F_5)_3$ with ROH compounds (R = H, alkyl, silaalkyl) affords $(C_6F_5)_3B \cdot OHR$, which acts as a Brønsted acid toward Cp'_2MMe_2 complexes [92]. The $[Cp'_2MMe][(C_6F_5)_3BOR]$ catalysts polymerize α-olefins to high molecular weight amorphous polymers.

Marks and co-workers have found that reaction of $Cp'MMe_2$ ($Cp' = Cp$, 1,2-Me_2Cp, or Cp*) or $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)MMe_2$ with tris(2,2′,2″-perfluorobiphenyl)boron (**33**) affords catalysts with greater activity than with $B(C_6F_5)_3$ (Table 3) [93]. This has been ascribed to the lower coordinating strength of the $[MeB(C_{12}F_9)_3]^-$ anion with respect to the $[MeB(C_6F_5)_3]^-$ anion. Whereas Cp'_2MMe_2 complexes and $B(C_6F_5)_3$ afford $[Cp'_2MMe][MeB(C_6F_5)_3]$ ion pairs, reaction of bis(cyclopentadienyl)metal dimethyl complexes with $B(C_{12}F_9)_3$ forms exclusively the methyl bridged dimers $[(Cp'_2MMe)_2(\mu\text{-}Me)][MeB(C_{12}F_9)_3]$ even in the presence of excess boron reagent.



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Preparation of an alternative neutral activator $Al(C_6F_5)_3$ by reaction of $AlCl_3$ with ethereal $[Ct][C_6F_5]$ ($Ct^+ = Li$) has hitherto been approached with caution due to the explosive nature of the $Al(C_6F_5)_3 \cdot$etherate product. An apparently safer preparation involves methathesis of $B(C_6F_5)_3$ and $AlMe_3$, $AlEt_3$, $Al(i\text{-}Bu)_3$, or $HAl(i\text{-}Bu)_2$ in aromatic or aliphatic solvents (Fig. 25). Yields of 70–90% of the unsolvated $Al(C_6F_5)_3$ have been obtained [94].

Table 3
Olefin polymerization by metallocene complexes cocatalyzed by $B(C_6F_5)_3$ and $B(C_{12}F_9)_3$

Catalyst	Monomer(s)[a]	Activity ($\times 10^5$)	M_W ($\times 10^3$)	M_W/M_N	Polymer characteristics
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=$	48.0	559	3.06	
$[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=$	40.0	124	2.03	
$[((1,2\text{-}Me_2C_5H_3)_2ZrMe)_2(\mu\text{-}Me)]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=$	78.0	392	2.72	
$[(1,2\text{-}Me_2C_5H_3)_2ZrMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=$	60.0	321	1.42	
$[((C_5Me_5)_2ZrMe)_2(\mu\text{-}Me)]^+[MeB(C_{12}F_5)_3]^-$	$C_2^=$	43.0	370	2.28	
$[(C_5Me_5)_2ZrMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=$	32.0	136	2.54	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)ZrMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=$	0	–	–	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)ZrMe]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=$	15.6	7.69	2.78	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=$	0.84	1058	9.54	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=$	49.8	305	2.56	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)ZrMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=/C_6^=$	0	–	–	
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)ZrMe]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=/C_6^=$	5.58	10.0	2.68	33.6% $C_6^=$
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe]^+[MeB(C_6F_5)_3]^-$	$C_2^=/C_6^=$	0.12	n.m.[b]	n.m.	63.2% $C_6^=$
$[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=/C_6^=$	4.68	105	1.86	65.3% $C_6^=$
$[(1,2\text{-}Me_2C_5H_3)TiMe_2]^+[MeB(C_6F_5)_3]^-$	$C_2^=/C_6^=$	1.70	848	23.7	39.5% $C_6^=$
$[(1,2\text{-}Me_2C_5H_3)TiMe_2]^+[MeB(C_{12}F_9)_3]^-$	$C_2^=/C_6^=$	10.8	151	4.32	43.6% $C_6^=$
$[(1,2\text{-}Me_2C_5H_3)TiMe_2]^+[MeB(C_{12}F_9)_3]^-$	Styrene	16.1	170	2.56	[rrrr]>98%
$[(1,2\text{-}Me_2C_5H_3)ZrMe_2]^+[MeB(C_{12}F_9)_3]^-$	Styrene	100	27.6	2.63	Atactic
$[(1,2\text{-}Me_2C_5H_3)HfMe_2]^+[MeB(C_{12}F_9)_3]^-$	Styrene	53.3	22.9	2.78	Atactic
$[(1,2\text{-}Me_2C_5H_3)HfMe_2]^+[MeB(C_6F_5)_3]^-$	Styrene	31.7	24.8	2.98	Atactic

[a] $C_2^=$, ethylene; $C_6^=$, 1-hexene.
[b] n.m., not measured.

$$B(C_6F_5)_3 + AlMe_3 \longrightarrow Al(C_6F_5)_3 + BMe_3$$

Fig. 25. Preparation of $Al(C_6F_5)_3$.

12. Structural and theoretical studies

Among the attractive features of metallocene olefin polymerization catalysts is that, unlike conventional Ziegler–Natta catalysts, the very same catalysts which polymerize olefins with commercially meaningful activities are ameable to comprehensive structural characterization and make an excellent basis for theoretical studies.

The reaction of $B(C_6F_5)_3$ with $Cp_2Ti^{13}CH_3Cl$ in toluene-d_8 affords two ionic species $[Cp_2TiCl]^+[MeB(C_6F_5)_3]^-$ and $[Cp_2TiMe]^+[ClB(C_6F_5)_3]^-$, as determined by ^{13}C-NMR [95]. Depending on the polarity of the solvent (adjusted by CD_2Cl_2), contact-ion pairs and solvent-separated ion-pairs are present.

With an excess of Cp'_2ZrMe_2 complexes, $B(C_6F_5)_3$ forms binuclear cations of the type $[(Cp'_2ZrMe)_2(\mu\text{-Me})][MeB(C_6F_5)_3]$ in equilibrium with the zirconocene dimethyl and the mononuclear cationic species, itself in equilibrium between contact ion pair and solvent-separated ion pair (Fig. 26) [96]. More sterically hindered zirconocenes such as $Cp^*_2ZrMe_2$ do not form binuclear complexes. The binuclear complex itself is not a catalyst for polymerization: the neutral zirconocene dimethyl must dissociate for polymerization to occur. Reaction of $Cp'_2Zr(CH_2CMe_3)_2$ with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ affords isobutane and the monomethyl complex $[Cp'_2ZrMe][A]$ by β-Me elimination; the neopentyl cation is not observed for $Cp' = Cp^*$, but when $Cp' = C_5H_5$ $[Cp_2ZrCH_2CMe_3]^+$ is stable at 0°C [97].

The reaction of $Cp'Zr(\eta\text{-PhC(NSiMe}_3)_2)Me_2$ ($Cp' = Cp$, Cp^*) with $B(C_6F_5)_3$ in dichloromethane affords a binuclear product with the zirconium atoms bridged by two chlorides: generation of the $[Zr]\text{–}Me^+$ cation is followed by abstraction of chloride from the solvent (Fig. 27) [98]. When benzene is used as the solvent, an active ethylene polymerization catalyst is formed, but the isolated product is the catalytically inactive $Cp'Zr(\eta\text{-PhC(NSiMe}_3)_2)(C_6F_5)(\mu\text{-Me})(B(C_6F_5)_3)$ formed by abstraction of a pentafluorophenyl group from the cocatalyst.

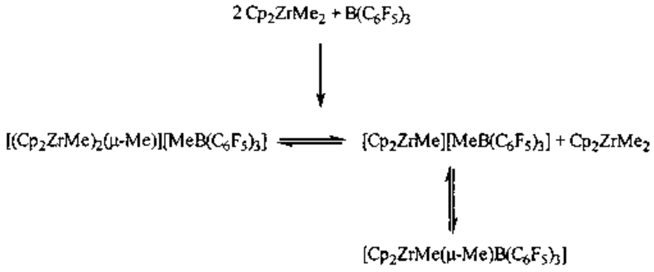


Fig. 26. Equilibrium reactions of Cp_2ZrMe_2 and $B(C_6F_5)_3$.

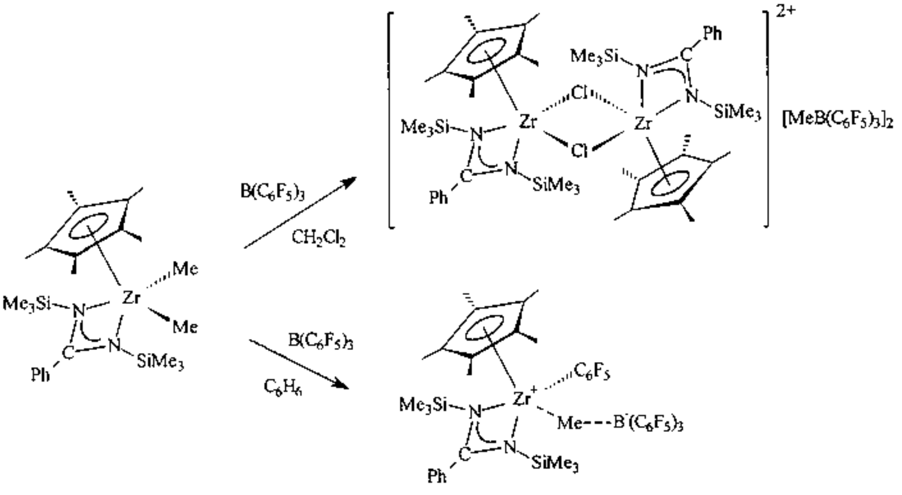


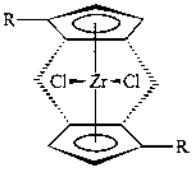
Fig. 27. Reactions of $Cp^*Zr(Me_3SiNC(Ph)NSiMe_3)Me_2$ with $B(C_6F_5)_3$.

The role of α-agostic interactions in metallocene polymerization catalysts was reviewed by Grubbs and Coates [99]. Isotopic effects on stereochemistry and reactions rates may be studied relatively straighforwardly by use of metallocene systems.

A study of the gas-phase reactions of Cp'_2ZrMe^+ cations with hydrogen, ethylene, propylene, and isobutylene shows that the electrophilicity of the metallocene cations decreases in the order $Cp_2ZrMe^+ > Cp(Ind)ZrMe^+ > (Ind)_2ZrMe^+ > (Flu)_2ZrMe^+$ [100]. Bridging of the two ancillary ligands by an Me_2Si group increases the electrophilicity somewhat, but activity does not necessarily correlate with electrophilicity, as the stability of the ion pair must also be considered.

Molecular modeling, X-ray crystallography, and ^{91}Zr-NMR were used correlate the polymerization activity of unbridged alkyl-substituted cyclopentadienyl- and phospholyl-zirconium complexes with structure [101]. The rate of ethylene polymerization is dependent on the relative openness of the active site, not the electronic effect of the substituents, with more sterically crowded zirconocenes (e.g. $Cp^*_2ZrCl_2$) less active than more open catalyst species, like that from Cp_2ZrCl_2. The phospholyl-based zirconocenes exhibited lower catalyst activity: aluminum complexation to the phosphorous atom renders the active site less accessible to monomer.

Cavallo and co-workers have investigated the feasibility of double-bridged metallocene complexes using quantum mechanical and molecular mechanics studies [102]. Examination of the C_2 complex **34** and the C_s complex **35** predicts that the former should be isospecific, though not as much so as the single-bridged complex with substituents in the distal positions, and the latter should be syndiospecific, a prognostication which has been borne out [32].



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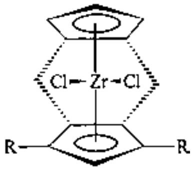

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An ab initio study of ethylene insertion into $H_2Si(Cp)_2ZrMe^+$ shows that there is essentially no barrer to insertion. Insertion takes place within 200 fs and is not dependent on temperature, with methyl group migration taking place at nearly the same rate when simulated at 50, 250, and 400 K [103]. Ethylene insertion into the analogous $H_2Si(Cp)_2TiMe^+$ complex is rather slower, taking place in about 500 fs. The same simulations on the mono(cyclopentadienyl) complexes $Me_2Si(Cp)(NEt)ZrMe^+$ and $Me_2Si(C_5Me_4)(NEt)TiMe^+$ indicate that no insertion takes place within the time scale of the simulation (900 fs) [104].

Comparing the insertion of ethylene into Cp_2ZrMe^+ and $Me_2Si(Cp)_2ZrMe^+$ by ab initio methods, the activation energy for insertion in the unbridged complex is lower than that for the bridged compound; the geometrical disposition of the molecular fragments appears to predominate over electronic considerations in explaining these differences [105]. Examining the insertion using density functional theoretical methods shows that the activation barrier to front-side insertion of ethylene is slightly less than that of back-side insertion (Fig. 28), both being lower

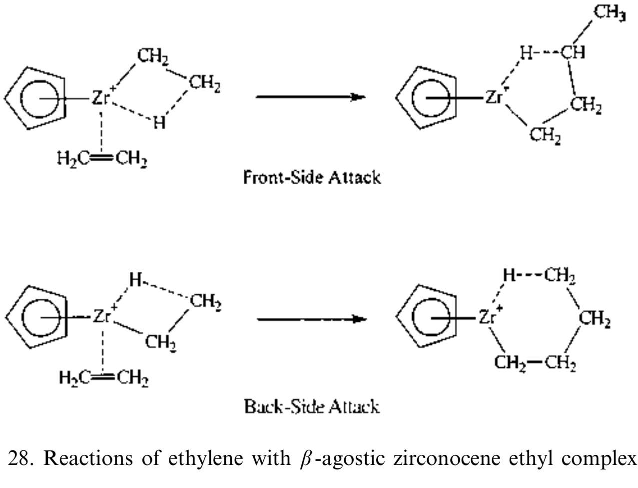


Fig. 28. Reactions of ethylene with β-agostic zirconocene ethyl complexes.

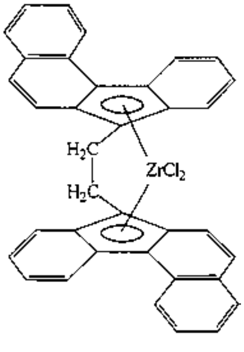
than that for hydride transfer. α-, β-, γ-, and δ-agostic interactions are present with the transition states shifting rapidly among them [106]. It has also been suggested that insertion of ethylene into the γ-agostic isomer of $Cp_2ZrC_3H_7^+$ forming a γ-agostic $Cp_2ZrC_5H_{11}^+$ product may be energetically comparable to insertion into the β-agostic reactant [107]. The resting state of a $H_2Si(Cp)(NH)TiR^+$ (R = propyl, butyl) interconverts between β- and γ-H agostic stabilized species, but the β-agostic interaction is preferred during ethylene insertion [108].

An combined ab initio-molecular mechanics study of propylene insertion into silyl-bridged C_2 symmetric metallocenes suggests that titanium complexes should afford the most isotactic material (at least at low temperatures) and that substitutents in the 2- and 4-positions of an indenyl ring are critical to improved stereoregulation [109]. A study of the isospecific complexes *rac*-Me_2Si(benz[*e*]indenyl)$_2ZrR^+$ and *rac*-Me_2Si(2-Me-benz[*e*]indenyl)$_2ZrR^+$ by molecular mechanics indicates that the presence of the 2-methyl substituent slows β-hydride transfer considerably, resulting in polymers of higher molecular weight [110].

13. Polymerization and copolymerizations of ethylene

Metallocene catalysts find special value in the copolymerization of ethylene with a variety of olefins. The excellent copolymerizing ability of most metallocene catalysts makes accessible ethylene copolymers of much lower densities than can be prepared with conventional Ziegler–Natta catalysts. The essentially random incorporation of comonomer and the narrow compositional distribution of the copolymer eliminates extractable low-molecular weight fractions.

While most metallocene catalysts are much more reactive to comonomers than conventional Ziegler–Natta systems, some metallocene catalysts are almost completely selective for ethylene polymerization. (Ind)(Cp*)$ZrCl_2$ polymerizes ethylene rapidly, but is inactive when exposed to propylene [111] and a *rac*/*meso* mixture of the bridged bis(benzofluorenyl)zirconium complex **36** similarly shows high activity in ethylene polymerizations but feeble performance when propylene is the monomer [112].



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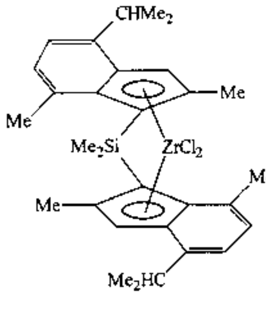
In a continuous gas-phase polymerization processes, metallocene catalysts tend to produce hydrogen gas, which functions as a chain-terminating agent; polymers of higher molecular weights are therefore difficult to achieve. Research at Exxon suggests that bis(cyclopentadienyl) metallocenes in which the total number of ring substituents is between four and eight (e.g. (Cp)(Cp*)$ZrCl_2$, $(MeBuCp)_2ZrCl_2$) form the desired high M_W copolymers without substantial loss of α-olefin copolymerization ability [113].

In EP or EPDM production, vanadium catalysts are preferred because of the narrow molecular weight distribution (MWD) of the polymer and random incorporation of comonomer. However, their activity is rather low and they tend to deactivate at elevated temperatures. On the other hand, metallocene-based catalysts produce random EP and EPDM at temperatures in excess of 100°C [114].

Dienes like ethylidenenorbornene (ENB) or dicyclopentadiene are frequently terpolymerized with ethylene and propylene to provide functionality for subsequent vulcanization. Non-conjugated dienes such as 5,7-dimethylocta-1,6-diene [115] and 7-methylocta-1,6-diene [116] are efficiently terpolymerized with ethylene and propylene (or higher α-olefins) by bridged bis(indenyl)zirconocenes at higher temperatures and activities than conventional vanadium-based catalysts. Trienes (e.g. 6,10-dimethylundeca-1,5,9-triene) and tetraenes (e.g. 5,9,13-trimethyltetradeca-1,4,8,12-tetraene) are also efficently terpolymerized by bridged and unbridged zirconocene–MAO catalysts [117].

Indenyl and fluorenyl metallocene complexes are customarily associated with stereospecific polymerizations, but they have proved useful in ethylene polymerizations as well. Dimethylsilyl-bridged bis(2-methylindenyl) zirconium complexes like **37** [118] and $Ph_2C(Cp)(Flu)ZrCl_2$ [119] can be used at high temperatures (120–170°C) to produce copolymers with higher molecular weights than those produced from $Me_2Si(Ind)_2ZrCl_2$ or Cp_2ZrCl_2 under similar conditions. Bis(2-methyl-4,5-benzoindenyl)zirconium dichloride copolymerizes ethylene and 1-hexene more efficiently, affording a lower density copolymer, than $(MeCp)_2ZrCl_2$ [120]. The bridged (indenyl)(fluorenyl) zirconium complex **38** also produces a more hexene-rich random copolymer than does $(n\text{-}BuCp)_2ZrCl_2$ [121].



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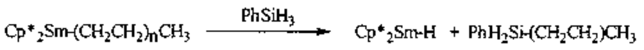
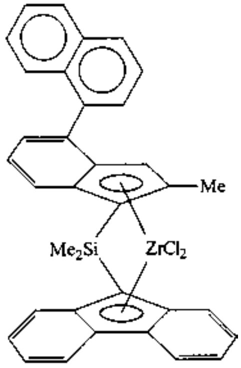


$$Cp^*_2Sm\text{-}(CH_2CH_2)_nCH_3 \xrightarrow{PhSiH_3} Cp^*_2Sm\text{-}H + PhH_2Si\text{-}(CH_2CH_2)CH_3$$

Fig. 29. Chain termination by $PhSiH_3$.



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Low molecular weight ethylene–butene copolymers produced from a $Me_2Si(H_4\text{-}Ind)_2ZrCl_2$–MAO catalyst at 90°C have microstructures in which the average polymer molecule has one unsaturated bond; these are predominantly vinylidene and trisubstituted olefin units in the ratio of 3:1. Butene is incorporated in a random manner with few blocks of ethylene or butene over two to three units long [122]. Even at low ethylene pressures (1 bar), Cp_2ZrMe_2–MAO affords solid linear polymers but liquid oligomers are produced in the presence of hydrogen or by addition of propylene [123]. Silanes like $PhSiH_3$ and $PhMeSiH_2$ also serve as chain-transfer agents for Cp_2^*SmH and $[Cp_2ZrMe][MeB(C_6F_5)_3]$ catalysts (Fig. 29) [124].

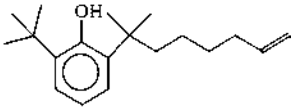
A number of studies have been conducted on the influence of the comonomer in copolymerzations of ethylene with linear 1-olefins. In copolymerizations at high temperatures (120–220°C) and pressures (1500 bar), activities of a $Me_2Si(H_4\text{-}Ind)_2ZrCl_2$–MAO catalyst activity decreased with greater comonomer concentration and reactivity decreased with increasing comonomer length [125]. At lower temperatures and pressures, the trend in comonomer reactivity is the same [126], but activity is less affected; polymer crystallinity correlates with comonomer incorporation, but not branch length [127]. The dependence of density, melting point, and heat of fusion on the extent of branching in ethylene copolymers with 1-octene, 1-tetradecene, and 1-octadecene produced from a Cp_2ZrCl_2–MAO catalyst is much stronger than comparable copolymers produced from a $TiCl_4$–$MgCl_2$–$AlEt_3$ catalyst; this may reflect the narrower comonomer distribution of polymers from metallocene catalysts [128].

The enhanced ability of metallocene catalysts, especially metallocenes like $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$ with relatively open active sites, to incorporate long-chain α-olefins also manifests itself in improved polymer processibility. Improvements in the onset of melt fracture in ethylene–octene copolymers produced from $[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe][RB(C_6F_5)_3]$ catalysts have been attributed to the presence of long-chain branching [129]. Mathematical models have been developed for the chain-length distributions under steady-state conditions [130]. Vinyl-terminated oligoethylenes ($M_N = 840$) appear to be incorporated by a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO catalyst, but are unreactive toward a Cp_2ZrCl_2–MAO system [131]. Bridged bis(cyclopentadienyl)zirconium-based catalysts may also form copolymers with long-chain branching: homo- and copolymers produced from $R_2C(Cp)(Flu)ZrCl_2$–MAO catalysts display rheological characteristics quite different than polymers from a $(n\text{-}BuCp)_2ZrCl_2$–MAO catalyst [132].

Because of its steric bulk, styrene is copolymerized with ethylene only with the greatest difficulty when conventional Ziegler–Natta catalysts are used. In contrast, metallocene catalysts are relatively effective for producing ethylene–styrene copolymers, especially those catalysts whose active sites are relatively open. $CpTiCl_3$–MAO [133] and $CpTi(CH_2Ph)_3$–$B(C_6F_5)_3$ [134] produce mixtures of polyethylene, ethylene–styrene copolymer, and syndiotactic polystyrene when exposed to a mixture of ethylene and styrene. Polyethylene is predominantly produced at 0°C while ethylene–styrene copolymer is the principal product at 50°C. The constrained-geometry catalyst $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO forms ethylene–styrene copolymers with styrene contents as high as 35 mol% without polystyrene impurities [135]. The styrene units are isolated or, at most, head-to-head coupled; blocks of polystyrene within the polymer chain are not formed. Ethylene, styrene, and ethylidene norbornene form terpolymers in the presence of constrained-geometry catalysts; these produce thermoset elastomers when crosslinked [136]. Bis(cyclopentadienyl)zirconium complexes copolymerize ethylene and styrene when the two rings are bridged; even so, *p*-methylstyrene is a more reactive comonomer than styrene when $Et(Ind)_2ZrCl_2$–MAO is the catalyst [137]. A related bulky monomer, 4-vinylcyclohexene, can be copolymerized with ethylene using a $Ph_2C(Cp)(Flu)ZrCl_2$–MAO catalyst; 4-VCH contents can range from 33 mol% (at 0°C) to 4 mol% (at 60°C) [138].

Functionalized polyolefins remain a desired goal in polymer synthesis, but the highly electrophilic early transition metal catalysts are quickly deactivated by polar groups. Ethylene and 10-undecene-1-ol are copolymerized by stereorigid zirconocenes such as $Me_2Si(Ind)_2ZrCl_2$ and Me_2Si(2-Me-4,5-benzoindenyl)$ZrCl_2$ [139]. Improvements in activity and incorporation come from complexation of the monomer with MAO and using elevated temperatures [140].

Copolymerization of ethylene with 6-*t*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol (**39**) using zirconocene/MAO catalysts affords a copolymer with a stabilizing additive directly incorporated into the chain [141]. The copolymers exhibit vastly improved oxidative stability over polymers with no bound stabilizer.



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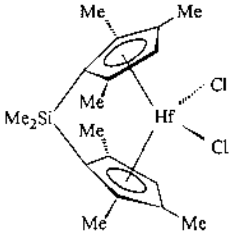
While metallocene catalysts produce polymers with narrow molecular weight distributions, in some applications (films, blow molding) a broader MWD is useful.

Two approaches have been disclosed to generating broad MWD polymers using metallocene catalysts. A combination of a bridged metallocene such as Et(Flu)$_2$-ZrCl$_2$ and an unbridged metallocene like (n-BuCp)$_2$ZrCl$_2$ produce a copolymer with a MWD of 21 [142]. Another route uses a single metallocene but mixtures of MAO and B(C$_6$F$_5$)$_3$ to give the broadened MWD [143].

14. Polymerization of propylene and higher α-olefins

A continuing goal in metallocene research is to discover a catalyst which produces isotactic polypropylene with a high melting point. While the number of *meso* placements may be very low, 2,1- and 1,3-misinsertions have a disproportionately heavy impact on the polymer melting point. Polymerization of propylene with the chiral bis(trimethylcyclopentadienyl) hafnium complex **40** largely suppresses these misinsertions and affords i-PP with melting points between 162 and 165°C [144]. The polymerization temperatures employed (20–30°C) were far below those used in commercial plants. The melting point of the polypropylene produced from a Et(Ind)$_2$ZrMe$_2$–[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst increases from 147.8 to 160.0°C when ethyl benzoate is used as an additive, but activities are greatly reduced [145]. Ethyl benzoate can also be used to induce isospecificity in an otherwise aspecific Cp′TiCl$_3$–MgCl$_2$–Al(i-Bu)$_3$ catalyst (Cp′ = Cp*, Ind, C$_9$Me$_7$) [146]. Again, catalyst activities are far lower than when no additive is used (by 85%) or in comparison to a TiCl$_4$–MgCl$_2$–EB catalyst (by 75%).



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Razavi has examined propylene polymerization by Me$_2$C(3-R-Cp)(Flu)ZrCl$_2$ catalysts. When R = t-Bu an isotactic polymer is formed (m.p. = 129°C, [mmmm] = 78.02%, [rrrr] = 0.28%); the back-skipping of the polymer chain after each insertion presents the incoming monomer with the same environment for the same enantioface to coordinate to the metal [147]. When R = Me$_3$Si, a predominantly isotactic polymer is formed, but the degree of isotacticity is reduced (m.p. = 105°C, [mmmm] = 66.57%) and the syndiotactic placements are increased ([rrrr] = 1.14%). This has been attributed to the formation of blocks of isotactic and syndiotactic segments caused by identical and alternating enantioface reaction [148]. The back-skipping of the polymer chain in α-olefin polymerizations by *ansa* metallocene catalysts has been analyzed using molecular mechanics [149]. Non-bonding interactions not only from groups on the cyclopentadienyl ring but also on the bridge substituents can have an effect on the stereospecificity of the catalyst.

At low propylene concentrations, Et(H_4-Ind)$_2$ZrCl$_2$–MAO produces substantially atactic polypropylene ([m] ≈ 0.60). However, polymerization of propylene deuterated at the 2-position yields isotactic polymer ([m] ≈ 0.85). This has been attributed to a kinetic isotope effect during the epimerization process which is believed to lead to *r* stereoirregularities (Fig. 30) [150].

Another view of error formation has been made by Chien, who holds that exchange of polymer chains between catalyst sites of opposite chirality gives rise to stereoerrors. The pure *S* enantiomer formed from Et(H_4-indenyl)$_2$Zr(O-acetyl-(*R*)-mandelate)$_2$ affords polypropylene of higher isotacticity with fewer regioirregularities and 1,3-insertions than the racemic mixture. Reducing catalyst concentration or immobilizing the catalyst on a support serve to improve stereospecificity.

The tacticity of the polypropylene produced by Me$_2$Si(N-*t*-Bu)(Flu)ZrCl$_2$ is strongly dependent on the cocatalyst used. When the metallocene is activated by Al(*i*-Bu)$_3$–MAO, syndiotactic polymer is produced ([rr] = 0.875), but when Al(*i*-Bu)$_3$–[Ph$_3$C][B(C$_6$F$_5$)$_4$] is used a substantially isotactic polymer results ([mm] = 0.951) [151]. The authors believe the inversion of stereocontrol is caused by the relative coordinating strength of the aluminum or boron anions with respect to the metallocene cation.

Unbridged metallocenes like (2-phenylindenyl)$_2$ZrCl$_2$ have attracted much interest because of their ability to prepare ‘elastomeric’ polypropylene with alternating atactic and isotactic blocks. This is caused by oscillation of the metallocene stereochemistry from *meso* to *rac* stereoisomers during the chain lifetime. The first disclosure of these catalysts was by Waymouth in 1995 [152]. Parallel research on these systems was carried out at Montell and a patent application filed before the publication date of Waymouth’s paper; the published application appeared in 1996 [153]. Another 2-substituted indenyl complex prepared by Chien and Rausch, (2-methylbenz[*e*]indenyl)$_2$ZrCl$_2$, produces atactic polypropylene even at 0°C [154]; clearly the steric bulk of the methyl group in the 2-position is insufficiently great to retard the librational motion of the indenyl ligands.

Bis(indenyl) zirconocenes substituted in the 1-position with terpenyl-based substituents like menthyl, neomenthyl, isomenthyl, and neoisomenthyl have been synthesized by Erker and coworkers [155]. Three torsional isomers were detected in the *rac* diastereomer (Fig. 31).

Polymerization of propylene by *rac*-(1-R-Ind)$_2$ZrCl$_2$ gave polymers of varying tacticities: when the R = menthyl or neoisomenthyl, substantially isotactic PP was

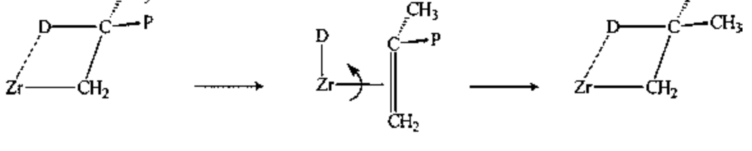

Fig. 30. Epimerization of the polypropylene chain in zirconocene catalysts.

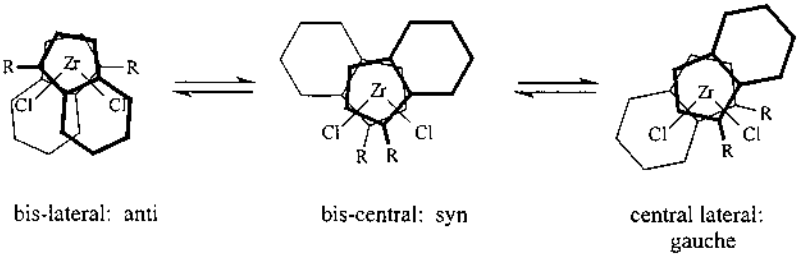

Fig. 31. Torsional isomers of $(3\text{-R-Ind})_2ZrCl_2$.

formed but atactic polymer was produced when R = neomenthyl or isomenthyl. In another study *meso*-like $(1\text{-}p\text{-tolyl-indenyl})_2ZrCl_2$ formed polypropylene with greater stereoregularity than that from the *rac* diastereomer [156].

Atactic polypropylene (a-PP) is usually thought of as a nuisance byproduct of isotactic propylene polymerization, but it can have its uses as a hot-melt adhesive or an additive. a-PP from conventional Ziegler–Natta catalysts is more properly poorly isotactic instead of amorphous. Fully atactic polypropylene with high molecular weight has been produced from $Me_2Si(Flu)_2ZrX_2$ complexes (X = Cl, Me) cocatalyzed by MAO [157]. The material is a non-sticky elastomer devoid of crystallinity. More active catalysts are obtained when the silylene group bears longer alkyl chains (C_4 and longer) [158]. Unbridged 2-substituted indenyl complexes of zirconium also give amorphous polymer of high molecular weight with high activity [159]. Low molecular weight propylene oligomers ($M_W = 1000–3000$), useful as precursors for lubricants and oil additives, are produced from achiral metallocenes combined with MAO [160].

Isospecific and aspecific metallocene catalysts have been used in tandem to produce thermoplastic elastomer blends with improved mechanical properties; the aspecific component, $Me_2Si(C_5Me_4)(N\text{-}c\text{-}C_{12}H_{23})TiCl_2$, is chosen to produce a higher molecular weight fraction than the isospecific component, e.g. $Me_2Si(H_4\text{-Ind})_2ZrCl_2$ [161]. Polypropylene waxes with reduced heats of fusion are produced from mixtures of diastereomers ($rac/meso < 0.5$) of *ansa*-metallocenes like $Me_2Si(2\text{-MeInd})_2ZrCl_2$ [162]. Polymerization of propylene with a $Et(Ind)_2ZrCl_2$/MAO catalyst co-supported on alumina with tetraneophylzirconium forms blends of isotactic and elastomeric polypropylene [163].

Alt and coworkers have made an extensive study of the effect bridging groups and fluorenyl ring substituents have on catalyst performance (Table 4) [164]. From these data, a number of points become clear:

- Hafnium complexes give s-PP of much higher molecular weight, but at lower activities.
- Diphenyl-substituted bridging groups afford polymers of much higher molecular weights than the dimethyl-substituted counterparts.
- Substitution of the fluorenyl ring in the 2- and 7-positions (**41**) have less of an effect on catalyst performance than does substitution in the 4- and/or 5-positions, where they interact most strongly with monomer and polymer chain to disrupt syndiospecificity.

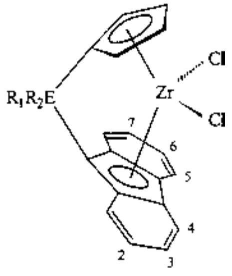

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Table 4
Propylene polymerization by $A(C_5H_4)(C_{13}H_{8-n}R_n)MCl_2$ complexes

A	R	M	Activity (kg PP mmol^{-1} Zr h^{-1})	m.p. (°C)	M_W ($\times 10^{-3}$)	Ref.
Me_2C	H	Zr	33.5	135.0	82	[165]c
Me_2C	2,7-Me_2	Zr	11.2	131.2	80	[165]c
Me_2C	4-Me	Zr	35.5	111.5	63	[165]c
Me_2C	4,5-Me_2	Zr	9.3	107.9	29	[165]c
Me_2C	3,4-Benzo	Zr	34.9	121.1	37.5	[165]c
Me_2C	4,5-Benzo	Zr	10.5	n.d.	154	[165]c
Me_2C	2,7-(Mesityl)$_2$	Zr	77.1	132.7	150	[165]c
Me_2C	2,7-Ph_2	Zr	17.6	132.5	80	[165]d
Me_2C	2,7-Cl_2	Zr	20.7	n.d.[a]	n.d.	[165]d
Me_2C	2,7-Br_2	Zr	26.8	131.0	60	[165]d
Me_2C	2,7-$(OMe)_2$	Zr	0.3	96.3	20	[165]d
Ph_2C	H	Zr	44.4	139	547	[165]c
Ph_2C	2,7-Me_2	Zr	34.7	134	330	[165]c
Ph_2C	4-Me	Zr	13.6	115.3	270	[165]c
Ph_2C	4,5-Me_2	Zr	6.0	139.1	230	[165]c
Ph_2C	3-*t*-Bu	Zr	47.5	144.8	530	[165]c
Ph_2C	2,7-(*t*-Bu)$_2$	Zr	31.8	136.4	310	[165]c
Ph_2C	2,7-(*t*-Bu)$_2$	Hf	13.7	138.4	850	[165]d
Ph_2C	2,7-$(PhMe_2C)_2$	Zr	72.7	115.0	520	[165]c
Ph_2C	3,4-Benzo	Zr	42.9	128.4	330	[165]c
Ph_2C	2-Ph	Zr	24.5	126.3	240	[165]d
Ph_2C	2,7-Ph_2	Zr	35.4	131.7	260	[165]d
Ph_2C	2,7-Ph_2	Hf	15.7	135.5	1200	[165]d
Ph_2C	2,7-Cl_2	Zr	41.0	129.6	175	[165]d
Ph_2C	2,7-$(OMe)_2$	Zr	0.4	116.1	<60	[165]d
HPhC	H	Zr	57.1	138.4	85	[165]b
$(CH_2)_4C$	H	Zr	35.3	132.0	110	[165]b
$(CH_2)_5C$	H	Zr	79.2	133.5	n.d.	[165]b
Me_2Si	H	Zr	25.4	76.18[b]	95.2	[165]a
Ph_2Si	H	Zr	117.4	74.45[b]	46.0	[165]a
Me_2Si	2,7-(*t*-Bu)$_2$	Zr	166.4	64.95[b]	96.1	[165]a
Ph_2Si	2,7-(*t*-Bu)$_2$	Zr	96.4	66.50[b]	113.6	[165]a
Ph_2Ge	H	Zr	8.28	65.46[b]	287.6	[165]a

[a] n.d., not determined.

[b] % [rr] triads.

Razavi's investigation of bridge substituent effects in methylene-bridged (cyclopentadienyl)(fluorenyl)zirconium dichlorides shows that use of *p*-substituted phenyl groups depresses catalyst activity and syndiospecificity with respect to the hydrocarbyl-bridged complexes, but improves the bulk density of the polypropylene produced [165].

Chien and Rausch prepared (t-Bu)CH(Cp)(Flu)$ZrCl_2$ which they used to polymerize propylene at temperatures from −20 to 60°C [166]. Molecular weights ranged from 199 000 to 61 000 and melting points of the syndiotactic polypropylene varied from 148 to 111°C. These investigators also undertook an examination of $Ph_2C(Cp)(Flu)ZrCl_2$ cocatalyzed by MAO and $Al(i\text{-}Bu)_3$–$[Ph_3C][B(C_6F_5)_4]$ [167]. Molecular weight and syndiospecificity were proportional to polymerization temperature and concentration of propylene; supporting the catalyst on silica did not affect the syndiospecificity.

Higher α-olefins can also be polymerized by metallocene catalysts. 3-Methyl-1-butene, a monomer frequently considered too bulky and unreactive for polymerization can form isotactic polymers when even simple C_2-symmetric metallocenes are used [168]. Curiously, the C_s-symmetric catalyst MePhC(Cp)(Flu)$ZrCl_2$ also affords what appears to be an isotactic polymer. This unusual results has been attributed to the back-skip of the chain coupled with chain-end control of stereospecificity.

Atactic polyhexene is produced by Cp'_2MCl_2 compounds cocatalyzed by MAO. Compression of the solution from 0.1 to 500 MPa results in a rise in polymer molecular weight and catalyst activity, but both enhancements are lost on a further increase to 1.5 GPa. The hafnocene $(C_5Me_4H)_2HfCl_2$ affords poly(1-hexene) with a molecular weight of over 3 000 000 [169]. The hafnocene $Et(Ind)_2HfCl_2$ copolymerizes propylene and higher α-olefins to give random copolymers ($r_1r_2 \approx 1$) [170]. The incorporation of comonomer by this catalyst is much higher than that of conventional Ziegler–Natta systems and indeed superior to the zirconocene analogue.

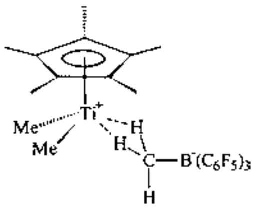
15. Polymerization of vinyl aromatic olefins

Syndiotactic polystyrene is a highly crystalline polymer with a high melting point (ca. 270°C) and high glass transition temperature. Its wide range of potential uses have led companies such as Dow and Idemitsu to begin commercialization of this material. The synthesis of s-PS by metallocene catalysts, especially thosed based on $Cp'TiX_3$ complexes, has been the subject of a recent review [171].

A series of experiments by Baird and co-workers examined the behavior of Cp^*TiMe_3 and $B(C_6F_5)_3$ in styrene polymerization [172]. At temperatures below 0°C, the ^1H-identifiable species $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ (**42**) is formed; this polymerizes ethylene at low temperatures, but forms only *atactic* polystyrene, indicating that it functions as a Ziegler–Natta catalyst toward ethylene but as a carbocationic initiator toward styrene. Above 0°C, the catalyst produces *syndiotactic* PS; this is accompanied by a weakening and broadening of the NMR signals of the catalyst solution. At room temperature, a Ti(III) species **43**, detected by ESR, is formed from Cp^*TiMe_3 and $B(C_6F_5)_3$ [173]; the formation of this complex is accelerated by addition of styrene to the mixture.

Table 5
Polymerization of styrene by $LTiCl_3$ catalysts

L	Activity ($\times 10^{-7}$)	s-PS (%)	M.p. (°C)	M_W ($\times 10^{-3}$)	Ref.
Cyclopentadienyl	1.4	67.4	259.7	435	[174]b
Indenyl	3.7	98.2	270.8	720	[174]b
Tetrahydroindenyl	2.7	89.1	270.9	620	[174]b
1-Methylindenyl	5.1	89.5	271.9	650	[174]b
2-Methylindenyl	16.6	90.2	272.2	660	[174]b
1-Ethylindenyl	2.6	82.0	272.3	430	[174]b
1-*t*-Butylindenyl	0.196	64.8	271.2	95	[174]b
1-Trimethylsilylindenyl	0.73	86.4	268.0	125	[174]b
1-Methylthioindenyl	0.183	80.5	268.1	14	[174]b
1-Phenylindenyl	7.7	90.0	260.7	424	[174]a
2-Phenylindenyl	5.2	91.3	262.5	323	[174]a
1,3-Diphenylindenyl	3.6	94.8	262.0	496	[174]a
1-Benzylindenyl	0.2	87.2	268.3	323	[174]a
3-(2-Phenylethyl)indene	1.1	88.2	267.8	401	[174]a
Benz[*e*]indenyl	17	92.5	270.4	545	[174]a
2-Methylbenz[*e*]indenyl	18	92.8	275.2	424	[174]a
1,2,3-Trimethylbenz[*e*]indenyl	2.0	96.0	276.0	323	[174]a



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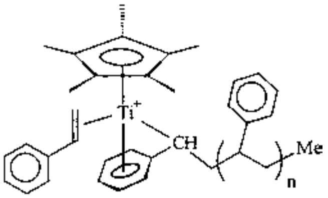

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Chien and Rausch have investigated a sizable number of indenyl derivatives of the formula $LTiCl_3$ in combination with MAO for their behavior in styrene polymerization (Table 5) [174]. Methyl substitution improves the activity of indenyl and benz[*e*]indenyltitanium trichloride, but ethyl and larger substituents depress catalyst activity. The methylthio derivative is virtually inactive, possibly from complexation of the lone pairs of electrons on the sulfur atom with MAO reversing the polarity of this substituent.

Octahydrofluorenyltitanium trichloride functions at least as effectively as Cp^*TiCl_3 in syndiotactic styrene polymerization [175] and $CpTiCl_2(O^iPr)$ has been claimed to be a more active and more stereospecific catalyst than $CpTiCl_3$ [176]. Bis(cyclopentadienyl)titanium and -zirconium derivatives activated by Ph_2Zn and MAO were also used to polymerize styrene [177]; here, however, conversions were low (1–9% of initial styrene) as were the butanone-insoluble fractions. Cp_2TiCl_2–Ph_2Zn–MAO produced the most syndiospecific catalyst, with 68% of the polymer formed insoluble in 2-butanone.

In order to reduce the amount of MAO used in the polymerization $CpTiCl_3$ has been supported on silica and used to polymerize styrene [178]. Highest activities result when the metallocene is supported, then activated with MAO rather than supporting the MAO and combining with the metallocene. Cp^*TiMe_3 has also been supported on silica and activated with $B(C_6F_5)_3$ in the presence of $Al(i\text{-}Bu)_3$ to form an active styrene polymerization catalyst [179].

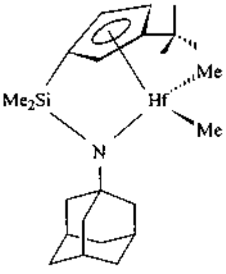
Syndiotactic polystyrene with a broad MWD is formed from mixtures of half-titanocenes (e.g. Cp^*TiMe_3 and $Cp^*Ti(OMe)_3$) activated by MAO [180]. $CpTiCl_3$–MAO catalysts also copolymerize styrene and vinyltoluenes to form syndiotactic terpolymers with melting points in the range of 210–240°C, lower than those of the homopolymer [181]. The molecular weight of s-PS can be controlled by using judicious amounts of alkylaluminum or alkylzinc compounds as chain-transfer agents [182].

Syndiotactic polystyrene can be produced in a continuous process without fouling by injection of monomer and catalyst ($Al(i\text{-}Bu)_3$ and MAO with $Cp^*Ti(OMe)_3$) into a continuously agitated and pulverized bed of s-PS [183]. Styrene has also been prepared in a reaction injection molding (RIM) process using a Cp^*TiMe_3–$B(C_6F_5)_3$ catalyst; the relatively low conversion of monomer (60–80%) under the conditions used is a limitation, however [184].

16. Polymerization and copolymerization of cyclic olefins

Metallocene catalysts readily polymerize and copolymerize cyclic olefins like cyclopentene and norbornene by an insertion, not a ring-opening, mechanism. The saturated polymers produced have very high glass transition temperatures, for the homopolymers in excess of 200°C. Amorphous ethylene copolymers of cyclic olefins find use as optical coatings for compact discs. Norbornene is commonly used as a comonomer for these copolymers, but the use of aryl-substituted cyclic olefins such as phenylnorbornene as comonomers or termonomers has been claimed to improve heat resistance and Shore hardness of the copolymer [185].

Ansa metallocenes like $Me_2C(Cp)(Flu)ZrCl_2$ with relatively open active sites are preferred for incorporating large amounts of cyclic olefin comonomer. C_1-symmetric monocyclopentadienyl amide complexes like the hafnium derivative **44** also avidly copolymerize norbornene [186]. Adjustments in the solubility parameters of the solvent used in the polymerization also affect the polymer characteristics [187]. For example, use of a toluene/hexane mixture as a reaction diluent affords an ethylene/norbornene copolymer with higher molecular weight and comonomer content than when either hydrocarbon is used alone [188].



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17. Polymerization of dienes and other olefinic monomers

The use of mono(cyclopentadienyl)vanadium complexes for butadiene polymerization has already been mentioned [71]. $CpTiCl_3$–MAO can also be used for the polymerization of butadiene and 4-methyl-1,3-pentadiene to 1,4-*cis*-polybutadiene and 1,2-syndiotactic poly(4-MP), respectively [189,190]. This catalyst is also capable of copolymerizing styrene and butadiene to SBR rubbers in a gas-phase polymerization [191]; astonishingly, ABS rubbers are produced as well from acrylonitrile, styrene, and butadiene.

Non-conjugated dienes like 1,7-octadiene are oligomerized by Cp_2ZrCl_2–MAO to chains containing internal vinylidene units [192]. This arises from incorporation of only one of the olefinic units into a chain, followed by termination, and reinsertion of an olefinic chain end (Fig. 32).

Exo-methylene polymers are also formed from the strained ring compounds methylenecyclopropane and methylenecyclobutane and $[Cp'_2ZrMe]^+[MeB(C_6F_5)_3]$ [193]. Lanthanide metallocenes and constrained-geometry metallocene cations are relatively ineffective. When $Cp' = Cp^*$, a polyspirane is formed from methylenecyclopropane caused by a ‘zipping-up’ of the *exo*-methylene polymer (Fig. 33).

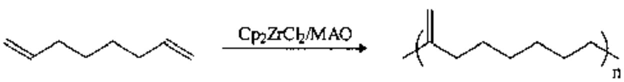

Fig. 32. Oligomerization of 1,7-octadiene by the zirconocene catalyst.

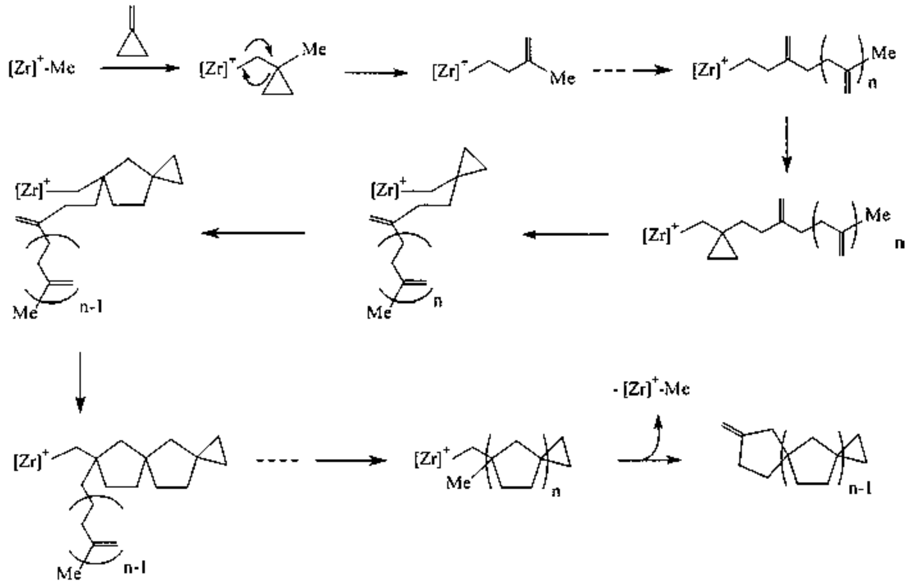

Fig. 33. Cyclopolymerization of methylenecyclopropane by zirconocene catalyst.

18. Supported metallocene catalysts

Solution polymerization processes are suitable for the preparation of low-crystallinity polyolefins such as elastomers, very-low-density ethylene copolymers, and amorphous poly-α-olefins. In these cases, the polymer product is soluble in the reaction medium and a solution-soluble catalyst system can be used.

Higher-crystallinity resins such as isotactic polypropylene or high-density polyethylene are usually prepared in continuous slurry, fluidized-bed gas phase, or bulk monomer processes. Here, the polymer is insoluble in the reaction medium. A morphologically uniform polymer particle is needed to avoid reactor fouling and facilitate smooth operations. Indeed, with proper control of catalyst and polymerizing conditions, polymer particles can be produced which can be directly used in fabrication processes like rotational molding without recourse to grinding or pelletizing [194].

Silica has been the most widely used support for metallocene catalysts, but other materials and methods for immobilizing the catalysts have been explored recently. Polypropylene produced by a $Et(Ind)_2ZrCl_2$–MAO catalyst confined within the pores of the zeolites MCM-41 and VPI-5 was found to be more stereoregular and of a higher molecular weight than that produced from the homogeneous catalyst [195]. Treatment of silica or alumina with 10–30 wt% boric acid has been claimed to lead to improvements in catalyst activity [196].

Metallocene catalysts have been assembled on the support material by impregnating silica with Group 4 tetrahalides and reacting with $Cp'–SiMe_3$ [197], Cp′Li [198],

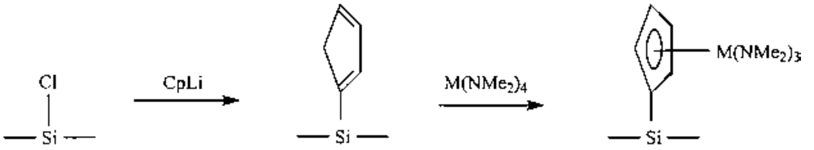

Fig. 34. Preparation of silica-supported cyclopentadienes.

or Cp'_2Mg [199] to afford a supported metallocene complex which can be activated by MAO or boron activators. Conversely, Cp′Li has been reacted with chlorinated silica giving silica with cyclopentadienyl groups attached. This material is then allowed to react with $M(NMe_2)_4$ (M = Ti, Zr) to form (silica)–$C_5H_4M(NMe_2)_3$ (Fig. 34) [200]. In a similar preparation, NaCp is allowed to react with ethylene–methyl acrylate copolymer to form what is presumed to be a keto-Cp intermediate (Fig. 35). Reaction of this species with $ZrCl_4(THF)_2$ or $CpZrCl_3$ forms a polymer-bound metallocene [201].

Lithiated polystyrene (LiPS) has been allowed to react with (Cp)(Flu)MeSiCl to form (Cp)(Flu)MeSi(PS). Deprotonation and reaction with $ZrCl_4$ affords a polymer-bound metallocene [202].

Catalysts affording polymers with narrow MWD's are formed from assembling metallocene components in the presence of silica. For example, combining $Zr(O^nPr)_4$, dimethylcyclopentadiene, $AlEt_3$, and MAO affords a catalyst mixture which, when supported on silica, polymerizes and copolymerizes ethylene and α-olefins to products with high bulk densities [203]. Terminal and internal olefins and acetylenes may also be added in the preparation step [204].

Incipient impregation by a catalyst solution of a porous support like silica has been used to reduce or eliminate reactor fouling. Metallocene and activator are added to the support in a volume of solution which just fills the pores of the support [205]. This method of addition maximizes the amount of catalyst within the pores of the support and minimizes the catalyst on the exterior or the support particle.

The ratio of the volume of catalyst solution to support pore volume that still avoids reactor fouling may be below 1 to less than 3-fold; the impregnated support should not form a slurry [206]. Anti-static agents have also been blended with the

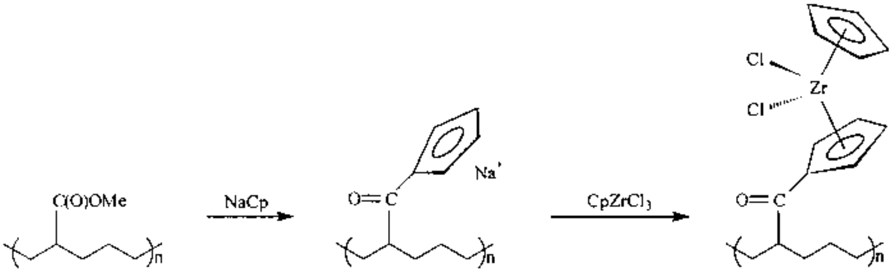

Fig. 35. Preparation of polymer-bound zirconocenes.

supported catalyst to reduce reactor fouling [207]. The solution can be sprayed onto the support with mixing in a conical mixer to ensure even combination [208] or added to the support by vacuum impregnation, wherein the support is stirred in a vacuum and the catalyst solution is injected [209]. The solid metallocene has also been dry-blended with the MAO–silica support at elevated temperatures [210].

One method of preparing supported metallocene–MAO catalysts has been to react $AlMe_3$ with hydrated silica to form surface-supported MAO. It has now been found that thorough washing of the supported MAO or the supported metallocene–MAO catalyst removes excess aluminum, resulting in significantly less fouling in slurry polymerizations of ethylene [211]. Heating the MAO–silica or metallocene–MAO–silica mixture is claimed to fix the catalyst to the silica surface, affording higher activites with less fouling [212]. Adjusting the CH_3/Al ratio in the MAO to 1.7–2.1 appears to improve supprted metallocene catalysts resulting in improved polymer fluidity and reduced fouling over MAO with Me/Al ratios above or below those limits [213].

Supported catalysts are sometimes prepolymerized to reduce fines production and increase polymer bulk density. However, high-activity supported metallocene catalysts can agglomerate in the prepolymerization step. Addition of hydrogen during the prepolymerization step controls this fouling and affords a morphologially uniform catalyst particle [214]. Drying the prepolymerized catalyst under a nitrogen stream to remove all entrained hydrocarbon solvent aids in adding the solid catalyst to fluidized-bed polymerization processes [215]. The supported catalyst may also be coated with low molecular weight, toluene-soluble polyolefins to slow the diffusion of monomer to the catalyst in the early stages of polymerization [216].

In gas-phase polymerization processes using conventional Ziegler–Natta catalysts, a trialkylaluminum reagent such as $AlEt_3$ is injected into the reactor to activate the catalyst and incidentally scavenge impurities from the gas stream. With metallocene-based catalysts, continuous addition of scavenger can result in fouling; injection beyond the start-up period is not recommended [217]. With these precautions, ethylene-α-olefin copolymers with very low densities—below 0.90 g cm^{-3}—have been obtained in a fluidized-bed gas-phase processes [218].

Conventional Ziegler–Natta catalysts and metallocene catalysts frequently respond quite differently to temperature, hydrogen, and comonomer concentration. In continuous polymerization processes, the transition from one catalyst to the other should be smooth and not require shutting down the reactor. Such a transition can be achieved by deactivation of the conventional Ziegler–Natta catalyst with CO_2 or wet silica before introducing the metallocene catalyst [219].

Ionic metallocene polymerization catalysts—ones not based on MAO—have been successfully supported. Pretreatment of a silica support with $AlEt_3$ removes potentially deactivating surface hydroxyl groups and allows an active silica-supported Cp'_2MMe_2–$[Ct][B(C_6F_5)_4]$ catalyst to be formed which can be used in slurry, gas-phase, or bulk-monomer processes [220]. Pretreatment of a silica support with $Al(i\text{-}Bu)_3$, supporting a mixture of metallocenes like $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$ or $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ combined with $Al(i\text{-}Bu)_3$, and activating with $B(C_6F_5)_3$ also affords an active catalyst system [221].

Reaction of supports such as silica, alumina, poly(vinylalcohol), and chloromethylated polystyrene with a base, followed by an fluororganic halide or tosylate like C_6F_5Br, provides an inert support for Cp'_2MMe_2–[Ct][$B(C_6F_5)_4$] or Cp'_2MMe_2–$B(C_6F_5)_3$ catalysts [222]. Catalysts for broad MWD polymers are prepared by reacting a chromium-impregnated alumina–silica support with a Cp_2ZrCl_2–$AlMe_3$–[Ph_3C][$B(C_6F_5)_4$] mixture [223].

Surface hydroxyl groups can be exploited in preparing a supported metallocene catalyst. Walzer has found that the reaction of $B(C_6F_5)_3$ with partially dehydroxylated silica forms $\equiv$Si–O(H)$B(C_6F_5)_3$, which, when combined with amine base, forms [R_3NH][$\equiv$Si–O$B(C_6F_5)_3$]. Reaction with a metallocene forms an active surface-supported ionic catalyst [224]. Reacting surface hydroxyl groups with BuLi, followed by treatment with $B(C_6F_5)_3$ forms Li[$\equiv$Si–O$B(C_6F_5)_3$], which can be allowed to react with Ph_3CCl to form the surface-bound ionic activator [Ph_3C][$\equiv$ Si–O$B(C_6F_5)_3$] [225]. Attachment of the non-interfering anion to the silica surface has also been achieved by the reaction of [$HNMe_2Ph$][4-$ClMe_2SiC_6H_4B(C_6F_5)_3$] with partially dehydroxylated silica [226] or [Et_3NH][$HOC_6H_4B(C_6F_5)_3$] with MAO-treated silica [227].

A supported activator with the cationic portion bound to silica was prepared by reacting *p*-$(MeO)_3SiC_6H_4NMe_2$ with partially hydroxylated silica to give a surface-bound amine $\{\equiv Si–O\}_3SiC_6H_4NMe_2$; protonation with HCl and reaction with [Li][$B(C_6F_5)_4$] gives a supported ionic activator [$\{\equiv Si–O\}_3SiC_6H_4NMe_2H$][$B(C_6F_5)_4$] [228].

19. Mixed metallocene–Ziegler catalysts

A perceived deficiency in polymers produced from metallocene catalyst is that their narrow molecular weight distribution makes processing more difficult. In order to overcome some of these problems, metallocene catalysts are sometimes used in conjunction with conventional Ziegler–Natta catalysts to produce polymers with broadened, but controllable MWD. Examples of such catalysts are $TiCl_4$–Bu_2Mg and (*n*-BuCp)$_2ZrCl_2$–MAO cosupported on silica [229], $Ti(OBu)_4$–$AlEt_3$ and Et(Ind)$_2ZrCl_2$–Al(*i*-Bu)$_3$ on $MgCl_2$ [230], Lynx®100 and (*n*-BuCp)$_2ZrCl_2$–MAO–$(MeOBO)_3$ [231], and $TiCl_4$–BuMeMg and (*n*-BuCp)$_2ZrCl_2$ on $AlMe_3$-treated hydrated silica [232]. Cp_2TiCl_2 has been used in the preparation of a $TiCl_4$–$Mg(OEt)_2$–dibutylphthalate catalyst for isotactic propylene polymerization [233], but it is not clear whether the titanocene is a polymerizing species or is simply an internal modifier for the conventional Ziegler–Natta catalyst.

Separately feeding to the reactor a silica-supported (*n*-BuCp)$_2ZrCl_2$–MAO catalyst along with the mixed system increases the low molecular weight fraction of the polymer blend [234]. Addition of water or carbon dioxide can help in modulating the weight fractions contributed by the two catalyst families [235].

Polymers with broad molecular weight distributions or multiple phases can also be prepared by polymerizing in a multistage process. Porous polypropylene produced from a conventional Ziegler–Natta catalyst was subsequently contacted with

$Et(Ind)_2ZrCl_2$ and MAO and used to copolymerize ethylene and propylene, thus producing an impact copolymer [236]. The same metallocene catalyst was used to polymerize ethylene and 1-butene at 180°C in a first reactor zone with a subsequent polymerization taking place in a second zone at 200°C using a conventional Ziegler–Natta catalyst [237].

20. Other process considerations

Aspects of reaction engineering in metallocene-catalyzed polymerizations, including polymer characterization and mathematical modelling, have been the subject of a recent review [238].

When the temperature at which a Cp_2ZrCl_2–MAO catalyst polymerizes ethylene is varied from -20 to 70°C, the activity increases moderately from 2800 to 83 000 kg PE mol cat^{-1} h^{-1} mol^{-1} $C_2^=$. A much greater increase to 250 000 is seen on raising the polymerization temperature to 90°C [239]. Polyethylene with a bimodal molecular weight distribution is produced when the temperature is raised from 10 to 80°C during the course of the polymerization. Raising the ethylene pressure in an ethylene–α-olefin copolymerization using a $Et(Ind)_2ZrCl_2$–MAO catalyst from 1.6 to 7.0 bar increases catalyst productivity (g PE mol Zr^{-1} h^{-1}) but depresses overall activity (g PE mol Zr^{-1} h^{-1} bar^{-1}); the crystallinity of the copolymer increases due to lower incorporation of comonomer [240].

The viscosity of an ethylene homopolymerization in heptane slurry using an $Et(Ind)_2ZrCl_2$–MAO catalyst increases rapidly even at low polymer concentrations. Addition of β-pinene effectively moderates this change in viscosity [241]. Reaction calorimetry has also been used with the same catalyst system in ethylene–α-olefin copolymerizations to measure heat transfer rates and copolymer compositions [242].

Increases in activity and comonomer reactivity in a silica-supported (n-$BuCp)_2ZrCl_2$–MAO catalyst have been observed when the polymerization is conducted at a temperature above the critical point of the propane diluent [243]. Adding dichloromethane to has been shown to increase the 1-hexene polymerization activity of a $Et(Ind)_2ZrCl_2$–MAO catalyst; this is attributed to a greater degree of charge separation in the ion pair. The use of CH_2Cl_2 as a diluent permits a lower amount of MAO to be used [244]. Addition of 2-methyl-1-butene to a metallocene–MAO catalyst solution is claimed to improve the activity of the catalyst; the reason for this effect was not disclosed [245].

References

[1] R. Lisowsky, US Patent 5,708,150 (1998), based on Eur. Pat. Appl. 718,303 (1996).
[2] J.Y. Lee, E.A. Burt, US Patent 5,569,746 (1996).
[3] J.Y. Lee, M.-S. Ao, S.E. Belmont, L.H. Shepherd, Jr., US Patent 5,648,583 (1997), based on Eur. Pat. Appl. 739,872 (1996).

[4] W.J. Layman, G.C. Robinson, US Patent 5,648,578 (1997), based on Eur. Pat. Appl. 739,874 (1996).

[5] Y. Matsumura, K. Suyama, Y. Inomata, Eur. Pat. Appl. 705,812 (1996).

[6] (a) L. Resconi, F. Piemontesi, I.E. Nifant'ev, P.V. Ivchenko, PCT Int. Appl. 96/22995 (1996). (b) I.E. Nifant'ev, P.V. Ivchenko, Eur. Pat. Appl. 722,949 (1996).

[7] (a) A.Z. Voskoboynikov, A.Yu. Agarkov, A.V. Churakov, L.G. Kuz'mina, Russ. Chem. Bull. 45 (1996) 726. (b) I.E. Nifant'ev, P.V. Ivchenko, L. Resconi, Eur. Pat. Appl. 722,950 (1996).

[8] B. Bildstein, P.M. Deinfl, R. Fleischanderl, E. Ernst, W. Neissl, Eur. Pat. Appl. 693,497 (1996).

[9] F. Aida, Y. Tajima, K. Matsuura, Eur. Pat. Appl. 714,920 (1996).

[10] W. Kaminsky, A.-M. Schauwienold, F. Freidanck, J. Mol. Catal. A 112 (1996) 37.

[11] Q. Yang, M.D. Jensen, Synlett (1996) 147.

[12] J.R. Strickler, J.M. Power, US Patent 5,556,997 (1996).

[13] R.A. Fisher, T.J. Burkhardt, PCT Int. Appl. 96/19488 (1996).

[14] F. Langhauser, D. Fischer, G. Schweier, H.H. Brintzinger, H.R.H. Damrau, Eur. Pat. Appl. 745,606 (1996).

[15] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.

[16] (a) J.N. Christopher, G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4038. (b) G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4045.

[17] W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, J. Organomet. Chem. 506 (1996) 351.

[18] D.W. Carpinetti, L. Kloppenberg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[19] H.-F. Herrmann, F. Küber, M. Aulbach, W.A. Herrmann, M. Morawietz, US Patent 5,726,333 (1998), based on Eur. Pat. Appl. 694,557 (1996).

[20] D.R. Wilson, US Patent 5,504,224 (1996).

[21] (a) H. Plenio, D. Burth, J. Organomet. Chem. 519 (1996) 269. (b) E. Barsties, S. Schaible, M.-H. Prosenc, U. Rief, W. Röll, O. Weyand, B. Dorer, H.-H. Brintzinger, J. Organomet. Chem. 520 (1996) 63. (c) H.J.G. Luttikhedde, R.P. Leino, C.-E. Wilén, J.H. Näsman, M.J. Ahlgrén, T.A. Pakkanen, Organometallics 15 (1996) 3092.

[22] R. Leino, H. Luttikhedde, C.-E. Wilén, R. Sillanpää, J.H. Näsman, Organometallics 15 (1996) 2450.

[23] F. Küber, M. Riedel, B. Bachmann, A. Winter, Eur. Pat. Appl. 743,317 (1996).

[24] M. Sone, S. Hasegawa, S. Yamada, A. Yano, Eur. Pat. Appl. 709,393 (1996).

[25] (a) P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, Chem. Ber. 129 (1996) 1509. (b) P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, Organometallics 15 (1996) 4153.

[26] (a) M. Mitani, M. Hayakawa, T. Yamada, T. Mukaiyama, Bull. Chem. Soc. Jpn. 69 (1996) 2967. (b) M. Mitani, K. Oouchi, M. Hayakawa, T. Yamada, T. Mukaiyama, Macromol. Chem. Phys. 197 (1996) 1815.

[27] M.W. Kim, E. Hong, T.K. Han, S.I. Woo, Y. Do, J. Organomet. Chem. 523 (1996) 211.

[28] T. Sugano, H. Uchino, K. Imaeda, E. Taniyama, N. Iwama, Eur. Pat. Appl. 697,418 (1996).

[29] (a) W.A. Herrmann, M.J.A. Morawietz, H.-F. Herrmann, F. Küber, J. Organomet. Chem. 509 (1996) 115. (b) H.-F. Herrmann, F. Küber, W.A. Herrmann, M. Morawietz, Eur. Pat. Appl. 742,225 (1996).

[30] (a) M. Aulbach, F. Küber, M. Riedel, F. Helmer-Metzmann, Eur. Pat. Appl. 749,985 (1996). (b) F. Helmer-Metzmann, F. Osan, M. Riedel, Eur. Pat. Appl. 749,988 (1996).

[31] D. Fischer, F. Langhauser, G. Schweier, H.-H. Brintzinger, N. Leyser, PCT Int. Appl. 96/26211 (1996).

[32] T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988.

[33] S. Mansel, U. Rief, M.-H. Prosenc, R. Kirsten, H.-H. Brintzinger, J. Organomet. Chem. 512 (1996) 225.

[34] T. Kashiwamura, N. Yabunouchi, M. Watanabe, N. Tani, T. Okamoto, K. Yokota, M. Kanezawa, T. Inoue, Eur. Pat. Appl. 818,458 (1998), based on PCT Int. Appl. 96/30380 (1996).

[35] K. Weiss, U. Neugebauer, S. Blau, H. Lang, J. Organomet. Chem. 520 (1996) 171.

[36] (a) H. Uchino, J. Endo, T. Takahama, T. Sugano, K. Katoh, N. Iwama, E. Taniyama, US Patent 5,594,081 (1997), based on Eur. Pat. Appl. 693,502 (1996). (b) T. Okamoto, M. Uemura, M. Watanabe, PCT Int. Appl. 96/04317 (1996). (c) L. Resconi, I.E. Nifant'ev, Y.A. Dubitsky, E. Barbassa, C. Schaverien, R. Ernst, PCT Int. Appl. 96/38458 (1996).

[37] S. Hamura, T. Yoshida, M. Sato, US Patent 5,770,666 (1998), based on Eur. Pat. Appl. 716,092 (1996).
[38] M. Aulbach, C. Fritze, H.-F. Herrmann, F. Küber, W. Spaleck, R. Zenk, Eur. Pat. Appl. 723,971 (1996).
[39] S.K. Noh, G. Byun, C. Lee, D. Lee, K. Yoon, K.S. Kang, J. Organomet. Chem. 518 (1996) 1.
[40] D. Lee, K. Yoon, S. Noh, S. Kim, Macromol. Rapid Commun. 17 (1996) 639.
[41] (a) T. Ushioda, M.L.H. Green, J. Haggitt, X. Yan, J. Organomet. Chem. 518 (1996) 155. (b) G.M. Diamond, A.N. Chernega, P. Mountford, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1996) 921.
[42] M. Aulbach, M.-J. Brekner, F. Küber, R. Zenk, Eur. Pat. Appl. 739,897 (1996).
[43] J.M. Canich, PCT Int. Appl. 96/00244 (1996).
[44] F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 245.
[45] Y. Aoyama, N. Tomotsu, Eur. Pat. Appl. 739,905 (1996).
[46] S. Nagy, R. Krishnamurti, J.A. Tyrell, L.V. Cribbs, M. Cocoman, US Patent 5,637,660 (1997), based on PCT Int. Appl. 96/33202 (1996).
[47] J.A.M. Van Beek, G.H.J. Van Doremaele, G.J.M. Gruter, H.J. Arts, G.H.M.R. Eggels, PCT Int. Appl. 96/13529 (1996).
[48] J.C. Flores, J.C.W. Chien, M.D. Rausch, Macromolecules 29 (1996) 8030.
[49] J.C. Flores, J.S. Wood, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 4944.
[50] Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, Can. J. Chem. 74 (1996) 1696.
[51] K. Frey, G. von Massow, H.G. Alt, M.B. Welch, US Patent 5,563,284 (1996).
[52] M. Riedel, F. Küber, M. Aulbach, G. Erker, M. Könemann, US Patent 5,750,752 (1998), based on Eur. Pat. Appl. 749,975 (1996).
[53] K. Kawai, T. Kitahara, T. Fujita, Jpn. Kokai Tokkyo Koho, JP 08/325315 (1996) (Chem. Abstr. 126 (1996) 144669).
[54] (a) D.D. Devore, F.J. Timmers, J.C. Stevens, R.K. Rosen, US Patent 5,486,632 (1996). (b) R.K. Rosen, D.D. Devore, US Patent 5,491,246 (1996). (c) R.K. Rosen, B.W.S. Kolthammer, US Patent 5,512,693 (1996). (d) F.J. Timmers, D.D. Devore, US Patent 5,527,929 (1996). (e) J.T. Patton, D.D. Devore, F.J. Timmers, J. Soto, G.F. Schmidt, D.R. Wilson, US Patent 5,543,480 (1996). (f) F.J. Timmers, D.D. Devore, J.C. Stevens, R.K. Rosen, J.T. Patton, D.R. Neithamer, PCT Int. Appl. 96/04290 (1996).
[55] B. Temme, J. Karl, G. Erker, Chem. Eur. J., 2 (1996) 919.
[56] (a) J. Ruwwe, G. Erker, R. Fröhlich, Angew. Chem. Int. Ed. Engl. 35 (1996) 80. (b) C. Fritze, H.-F. Herrmann, G. Erker, J. Ruwwe, Eur. Pat. Appl. 748,821 (1996).
[57] W.T. Reichle, F.J. Karol, G.T. Whiteker, US Patent 5,527,752 (1996).
[58] I. Kim, R.F. Jordan, Macromolecules 29 (1996) 489.
[59] B. Peifer, H.G. Alt, M.B. Welch, US Patent 5,654,475 (1997), based on Eur. Pat. Appl. 745,607 (1996).
[60] F. Lindenberg, T. Shribman, J. Sieler, E. Hey-Hawkins, M.S. Eisen, J. Organomet. Chem. 515 (1996) 19.
[61] J. Wünsch, W. Meier, PCT Int. Appl. 96/26226 (1996).
[62] J. Wünsch, M. Lux, D. Fischer, PCT Int. Appl. 96/26227 (1996).
[63] S.-J. Wang, Y.-C. Chen, S.-H. Chan, J.-C. Tsai, Y.-H.E. Sheu, US Patent 5,519,099 (1996).
[64] (a) B.P. Etherton, S. Nagy, US Patent 5,539,124 (1996). (b) H. Katayama, T. Watanabe, A. Imai, Eur. Pat. Appl. 741,145 (1996).
[65] R. Krishnamurti, S. Nagy, B.P. Etherton, US Patent 5,554,775 (1996).
[66] S. Nagy, R. Krishnamurti, B.P. Etherton, PCT Int. Appl. 96/34021 (1996).
[67] D.R. Wilson, D.R. Neithamer, P.N. Nickias, W.J. Kruper, Jr., US Patent 5,541,349 (1996).
[68] D.R. Wilson, G.F. Schmidt, PCT Int. Appl. 96/16094 (1996).
[69] Y. Liang, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Organometallics 15 (1996) 5284.
[70] D.L. Beach, M.J. Carney, J.M. Mora, PCT Int. Appl. 96/23006 (1996).
[71] G. Ricci, A. Panagia, L. Porri, Polymer 37 (1996) 363.
[72] J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045.
[73] J.H. Gilchrist, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 12021.

[74] J.-F. Pelletier, A. Mortreaux, X. Olonde, K. Bujadoux, Angew. Chem. Int. Ed. Engl. 35 (1996) 1854.

[75] E. Ihara, M. Nodono, H. Yasuda, N. Kanehisa, Y. Kai, Macromol. Chem. Phys. 197 (1996) 1909.

[76] S. Ya. Knjazhanski, A.I. Sizov, A.V. Khvostov, B.M. Bulychev, Russ. Chem. Bull. 45 (1996) 1745.

[77] R. Taube, S. Maiwald, J. Sieler, J. Organomet. Chem. 513 (1996) 37.

[78] D.P. Long, P.A. Bianconi, J. Am. Chem. Soc. 118 (1996) 12453.

[79] S.S. Reddy, Polym. Bull. (Berlin) 36 (1996) 317.

[80] T. Dall'Occo, M. Galimberti, L. Resconi, E. Albizzati, G. Pennini, PCT Int. Appl. 96/02580 (1996).

[81] S.S. Reddy, K. Radhakrishnan, S. Sivaram, Polym. Bull. (Berlin) 36 (1996) 165.

[82] A.N. Speca, US Patent 5,552,358 (1996).

[83] R.L. Geerts, M.B. Welch, S.J. Palackal, H.R. Deck, H.G. Alt, B. Peifer, US Patent 5,670,589 (1997), based on Eur. Pat. Appl. 726,271 (1996).

[84] S.A. Sangokoya, M.S. Howie, P.G. Simms, K.E. Wiegand, US Patent 5,565,395 (1996).

[85] J. Jin, T. Uozumi, K. Soga, Macromol. Chem. Phys. 197 (1996) 849.

[86] D.D. Devore, D.R. Neithamer, R.E. LaPointe, R.D. Mussell, US Patent 5,625,087 (1997), based on PCT Int. Appl. 96/08519 (1996).

[87] K. Yamamoto, K. Wakatsuki, H. Hozumi, A. Furusawa, Eur. Pat. Appl. 708,117 (1996).

[88] M. Ono, S. Hinokuma, S. Miyake, S. Inazawa, Eur. Pat. Appl. 710,663 (1996).

[89] W.E. Piers, R.E. von H. Spence, US Patent 5,496,960 (1996).

[90] N.L. Krzystowczyk, S.P. Diefenbach, W.L. Lemoine, US Patent 5,693,261 (1997), based on Eur. Pat. Appl. 728,760 (1996).

[91] S.P. Diefenbach, US Patent 5,600,004 (1997), based on Eur. Pat. Appl. 728,761 (1996).

[92] A.R. Siedle, J.A. Miller, W.M. Lamanna, PCT Int. Appl. 96/26967 (1996).

[93] Y.-X. Chen, C.L. Stern, S. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 12451.

[94] P. Biagini, G. Lugli, L. Abis, P. Andreussi, US Patent 5,602,269 (1997), based on Eur. Pat. Appl. 694,548 (1996).

[95] I. Tritto, P. Locatelli, M.C. Sacchi, S.X. Li, G. Zannoni, Gazz. Chim. Ital. 126 (1996) 383.

[96] S. Beck, M.-H. Prosenc, H.-H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, J. Mol. Catal. A 111 (1996) 67.

[97] A.D. Horton, Organometallics 15 (1996) 2675.

[98] R. Gómez, M.L.H. Green, J.L. Haggitt, J. Chem. Soc. Dalton Trans. (1996) 939.

[99] R.H. Grubbs, G.W. Coates, Acc. Chem. Res. 29 (1996) 85.

[100] D.E. Richardson, N.G. Alameddin, M.F. Ryan, T. Hayes, J.R. Eyler, A.R. Siedle, J. Am. Chem. Soc. 118 (1996) 11244.

[101] C. Janiak, K.C.H. Lange, U. Versteeg, D. Lentz, P.H.M. Budzelaar, Chem. Ber. 129 (1996) 1517.

[102] L. Cavallo, P. Corradini, G. Guerra, L. Resconi, Organometallics 15 (1996) 2254.

[103] G.H.J. van Doremaele, R.J. Meier, S. Iarlori, F. Buda, Theochem 363 (1996) 269.

[104] S. Iarlori, F. Buda, R.J. Meier, G.H.J. van Doremaele, Mol. Phys. 87 (1996) 801.

[105] V.L. Cruz, A. Muñoz-Escalona, J. Martinez-Salazar, Polymer 37 (1996) 1663.

[106] P. Margl, J.C.W. Lohrenz, T. Ziegler, P.E. Blöchl, J. Am. Chem. Soc. 118 (1996) 4434.

[107] J.A. Støvneng, E. Rytter, J. Organomet. Chem. 519 (1996) 277.

[108] T.K. Woo, P.M. Margl, J.C.W. Lorenz, P.E. Blöchl, T. Ziegler, J. Am. Chem. Soc. 118 (1996) 13021.

[109] T. Yoshida, N. Koga, K. Morokuma, Organometallics 15 (1996) 766.

[110] L. Cavallo, G. Guerra, Macromolecules 29 (1996) 2729.

[111] (a) M.A. Schmid, H.G. Alt, W. Milius, J. Organomet. Chem. 514 (1996) 45. (b) M. Schmid, H.G. Alt, M.B. Welch, US Patent 5,541,272 (1996).

[112] H.G. Alt, R. Zenk, J. Organomet. Chem. 512 (1996) 51.

[113] H.C. Welborn, Jr., J.F. Walzer, Jr., V.R. Sagar, E.E. Poirot, J.M. Canich, T.J. Burkhardt, PCT Int. Appl. 96/00246 (1996).

[114] R.S. Schiffino, J.M. Zamora, US Patent 5,696,213, based on PCT Int. Appl. 96/33227 (1996).

[115] M. Dolatkhani, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 197 (1996) 2481.

[116] (a) T. Sagane, T. Tsutsui, M. Kawasaki, K. Okada, T. Tojo, T. Tanizaki, US Patent 5,610,254 (1997), based on Eur. Pat. Appl. 718,324 (1996). (b) T. Sagane, T. Tsutsui, M. Kawasaki, K. Okada, H. Nakahama, T. Tojo, US Patent 5,696,214, based on Eur. Pat. Appl. 718,325 (1996).
[117] T. Sagane, M. Kawasaki, H. Nakahama, T. Ishida, K. Takahashi, T. Tsutsui, H. Onishi, M. Yasuda, N. Kihara, Eur. Pat. Appl. 691,354 (1996).
[118] T. Tsutsui, T. Sagane, Eur. Pat. Appl. 745,615 (1996).
[119] M. Sone, S. Hasegawa, S. Yamada, A. Yano, Eur. Pat. Appl. 709,405 (1996).
[120] H.-F. Herrmann, M. Aulbach, F. Küber, US Patent 5,670,436 (1997), based on Eur. Pat. Appl. 707,010 (1996).
[121] Y. Okamura, N. Kibino, T. Maki, A. Hori, K. Ishida, S. Miyake, S. Inazawa, US Patent 5,770,664 (1998), based on Eur. Pat. Appl. 707,016 (1996).
[122] A. Rossi, J. Zhang, G. Odian, Macromolecules 29 (1996) 2331.
[123] M. Michelotti, A. Altomare, F. Ciardelli, P. Ferrarini, Polymer 37 (1996) 5011.
[124] T.J. Marks, P.-F. Fu, US Patent 5,578,690 (1996).
[125] C. Bergemann, R. Cropp, G. Luft, J. Mol. Catal. A 105 (1996) 87.
[126] G.B. Galland, R. Quijada, R.S. Mauler, S.C. de Menezes, Macromol. Rapid Commun. 17 (1996) 607.
[127] R. Quijada, G.B. Galland, R.S. Mauler, Macromol. Chem. Phys. 197 (1996) 3091.
[128] J. Koivumäki, Polym. Bull. 36 (1996) 7.
[129] S.-Y. Lai, J.R. Wilson, G.W. Knight, J.C. Stevens, P.-W.S. Chum, PCT Int. Appl. 96/07680 (1996).
[130] J.B.P. Soares, A.E. Hamielec, Macromol. Theory Simul. 5 (1996) 547.
[131] K. Soga, T. Uozumi, S. Nakamura, T. Toneri, T. Teranishi, T. Sano, T. Arai, Macromol. Chem. Phys. 197 (1996) 4237.
[132] H.G. Alt, S.J. Palackal, M.B. Welch, D.C. Rohlfing, J. Janzen, B. Peifer, US Patent 5,710,224 (1998), based on Eur. Pat. Appl. 729,978 (1996).
[133] L. Oliva, S. Mazza, P. Longo, Macromol. Chem. Phys. 197 (1996) 3115.
[134] C. Pellecchia, D. Pappalardo, M. D'Arco, A. Zambelli, Macromolecules 29 (1996) 1158.
[135] F.G. Sernetz, R. Mülhaupt, R.M. Waymouth, Macromol. Chem. Phys. 197 (1996) 1071.
[136] K.W. McKay, F.J. Timmers, E.R. Feig, PCT Int. Appl. 96/07681 (1996).
[137] T.C. Chung, H.L. Lu, US Patent 5,543,484 (1996).
[138] W. Kaminsky, D. Arrowsmith, H.R. Winkelbach, Polym. Bull. 36 (1996) 577.
[139] P. Aaltonen, G. Fink, B. Löfgren, J. Seppälä, Macromolecules 29 (1996) 5255.
[140] P. Aaltonen, B. Löfgren, J. Seppälä, PCT Int. Appl. 96/34023 (1996).
[141] C.-E. Wilén, H. Luttikhedde, T. Hjertberg, J.H. Näsman, Macromolecules 29 (1996) 8569.
[142] M.B. Welch, R.L. Geerts, S.J. Palackal, T.M. Pettijohn, US Patent 5,534,473 (1996).
[143] W. Michiels Vega, A. Munoz-Escalona, Eur. Pat. Appl. 719,797 (1996).
[144] J. Saito, N. Kawamoto, A. Kageyama, Y. Oogi, K. Hatada, Eur. Pat. Appl. 748,824 (1996).
[145] H. Deng, K. Soga, Polym. Bull. (Berlin) 37 (1996) 29.
[146] K. Soga, Y. Suzuki, T. Uozumi, E. Kaji, J. Polym. Sci. Polym. Chem. 35 (1996) 291.
[147] A. Razavi, J.L. Atwood, J. Organomet. Chem. 520 (1996) 115.
[148] A. Razavi, Eur. Pat. Appl. 747,406 (1996).
[149] G. Guerra, L. Cavallo, G. Moscardi, M. Vacatello, P. Corradini, Macromolecules 29 (1996) 4834.
[150] V. Busico, L. Caporaso, R. Cipullo, L. Landriani, G. Angelini, A. Margonelli, A.L. Segre, J. Am. Chem. Soc. 118 (1996) 2105.
[151] T. Shiomura, T. Asanuma, N. Inoue, Macromol. Rapid Commun. 17 (1996) 9.
[152] G.W. Coates, R.M. Waymouth, Science 267 (1995) 217.
[153] L. Resconi, F. Piemontesi, L.-C. Yu, US Patent 5,747,621 (1998), based on PCT Int. Appl. 96/20225 (1996).
[154] P. Foster, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 4951.
[155] M. Knickmeier, G. Erker, T. Fox, J. Am. Chem. Soc. 118 (1996) 9623.
[156] T.K. Han, S.C. Yoon, Y.S. Ko, B.W. Woo, J.T. Park, S.I. Woo, Polym. Bull. 37 (1996) 35.
[157] L. Resconi, R.L. Jones, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 998.
[158] L. Resconi, R.L. Jones, Eur. Pat. Appl. 729,968 (1996).

[159] L. Resconi, F. Piemontesi, D. Balboni, Eur. Pat. Appl. 693,506 (1996).

[160] (a) S. Seelert, H.-J. Müller, B.L. Marczinke, F. Langhauser, C. Janiak, PCT Int. Appl. 96/23750 (1996). (b) J. Rösch, H.-J. Müller, G. Schweier, P. Tanzmeier, PCT Int. Appl. 96/23751 (1996).

[161] J.M. Canich, H.W. Yang, G.F. Licciardi, US Patent 5,516,848 (1996).

[162] H.-F. Herrmann, Eur. Pat. Appl. 719,802 (1996).

[163] E. Ernst, J. Reussner, W. Neissl, Eur. Pat. Appl. 695,765 (1996).

[164] (a) K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63. (b) H.G. Alt, R. Zenk, J. Organomet. Chem. 518 (1996) 7. (c) H.G. Alt, R. Zenk, W. Milius, J. Organomet. Chem. 514 (1996) 257. (d) H.G. Alt, R. Zenk, J. Organomet. Chem. 522 (1996) 39.

[165] A. Razavi, D. Vereecke, PCT Int. Appl. 96/16069 (1996).

[166] J.C.W. Chien, M.D. Rausch, US Patent 5,525,690 (1996).

[167] W. Song, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Polym. Chem. 34 (1996) 2945.

[168] A. Borriello, V. Busico, R. Cipullo, J.C. Chadwick, O. Sudmeijer, Macromol. Rapid Commun. 17 (1996) 589.

[169] A. Fries, T. Mise, A. Matsumoto, H. Ohmori, Y. Wakasuki, J. Chem. Soc. Chem. Commun. (1996) 783.

[170] M. Arnold, O. Henschke, J. Knorr, Macromol. Chem. Phys. 197 (1996) 563.

[171] R. Po', N. Cardi, Prog. Polym. Sci. 21 (1996) 47.

[172] Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693.

[173] A. Grassi, A. Zambelli, F. Laschi, Organometallics 15 (1996) 480.

[174] (a) P. Foster, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 2404. (b) T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 519 (1996) 21.

[175] P.N. Nickias, K.K. Borodychuk, T.H. Newman, US Patent 5,536,797 (1996).

[176] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polym. Bull. 37 (1996) 719.

[177] F.M. Rabagliati, R. Quijada, M.V. Cuevas, C.A. Terraza, Polym. Bull. 37 (1996) 13.

[178] J.-H. Yim, K.-J. Chu, K.-W. Choi, S.-K. Ihm, Eur. Polym. J. 32 (1996) 1381.

[179] J. Wünsch, D. Fischer, PCT Int. Appl. 96/29353 (1996).

[180] J. Wünsch, D. Fischer, M. Lux, D. Lilge, PCT Int. Appl. 96/20226 (1996).

[181] R. Po', N. Cardi, Eur. Pat. Appl. 745,619 (1996).

[182] H. Teshima, N. Tomotsu, US Patent 5,739,227 (1998), based on Eur. Pat. Appl. 742,233 (1996).

[183] J.H. Sliddall, D.A. Beaudoin, US Patent 5,484,862 (1996).

[184] T.M. Liu, W.E. Baker, V. Schytt, T. Jones, M.C. Baird, J. Appl. Polym. Sci. 62 (1996) 1807.

[185] C. Bergström, J. Seppälä, J. Ruotoistenmäki, T. Hase, S. Paavola, L.-O. Pietilä, L. Ahjopalo, PCT Int. Appl. 96/35730 (1996).

[186] B.A. Harrington, US Patent 5,621,054, based on PCT Int. Appl. 96/40806 (1996).

[187] Y. Abe, T. Sagane, Eur. Pat. Appl. 729,983 (1996).

[188] Y. Abe, T. Sagane, US Patent 5,650,471, based on Eur. Pat. Appl. 719,803 (1996).

[189] G. Ricci, C. Bosisio, L. Porri, Macromol. Rapid Commun. 17 (1996) 781.

[190] P. Longo, A. Proto, P. Oliva, A. Zambelli, Macromolecules 29 (1996) 5500.

[191] K.J. Cann, M.A. Apecetche, J.H. Moorhouse, N. Muruganandam, G.G. Smith, G.H. Williams, PCT Int. Appl. 96/04322 (1996).

[192] J. Christoffers, R.G. Bergman, J. Am. Chem. Soc. 118 (1996) 4715.

[193] (a) L. Jia, X. Yang, S. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 1547. (b) L. Jia, X. Yang, A.M. Seyam, I.D.L. Albert, P.-F. Fu, S. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 7900. (c) T.J. Marks, X. Yang, L. Jia, US Patent 5,480,952 (1996).

[194] K. Kallio, U. Palmqvist, H. Knuuttilla, A.M. Fatnes, PCT Int. Appl. 96/34898 (1996).

[195] Y.S. Ko, T.K. Han, J.W. Park, S.I. Woo, Macromol. Rapid Commun. 17 (1996) 749.

[196] T. Sugano, K. Yamamoto, Eur. Pat. Appl. 728,773 (1996).

[197] D.G. Ward, P. Brems, PCT Int. Appl. 96/13532 (1996).

[198] R. Spitz, V. Pasquet, J. Dupuy, J. Malinge, US Patent 5,739,226 (1998), based on Eur. Pat. Appl. 708,116 (1996).

[199] D.G. Ward, PCT Int. Appl. 96/13531 (1996).

[200] L. Gila, A. Proto, E. Ballato, D. Vigliarolo, G Lugli, Eur. Pat. Appl. 725,086 (1996).

[201] A.J. DiMaio, US Patent 5,587,439 (1996).
[202] (a) B. Peifer, H.G. Alt, M.B. Welch, S.J. Palackal, US Patents 5,492,973, 5,492,974, and 5,492,975 (1996). (b) B. Peifer, H.G. Alt, S.J. Palackal, US Patent 5,492,985 (1996).
[203] (a) Y. Tajima, N. Kataoka, A. Sano, K. Matsuura, Eur. Pat. Appl. 694,563 (1996). (b) H. Shimizu, A. Sano, K. Matsuura, US Patent 5,750,454 (1998), based on Eur. Pat. Appl. 745,616 (1996).
[204] T. Seki, A. Sano, K. Matsuura, Y. Tajima, Eur. Pat. Appl. 748,823 (1996).
[205] F.Y.-K. Lo, T.E. Nowlin, R.S. Shinmoto, P.P. Shirodkar, US Patent 5,602,067 (1997), based on PCT Int. Appl. 96/14155 (1996).
[206] (a) A.N. Speca, J.L. Brinen, G.A. Vaughn, P. Brant, T.J. Burkhardt, PCT Int. Appl. 96/00243 (1996). (b) G.A. Vaughn, A.N. Speca, P. Brant, J.M. Canich, PCT Int. Appl. 96/00245 (1996).
[207] (a) A.K. Agapoiu, M.E. Muhle, A.N. Speca, PCT Int. Appl. 96/11960 (1996). (b) A.N. Speca, J.L. Brinen, PCT Int. Appl. 96/11961 (1996).
[208] J.L. Brinen, A.N. Speca, K. Tormaschy, K.A. Russell, US Patent 5,625,015 (1997).
[209] M. Chang, PCT Int. Appl. 96/18661 (1996).
[210] H. Knuuttila, H. Hokkanen, E. Salo, PCT Int. Appl. 96/32423 (1996).
[211] M. Chang, PCT Int. Appl. 96/04318 (1996).
[212] (a) G.B. Jacobsen, L. Spencer, P.L. Wauteraerts, PCT Int. Appl. 96/16092 (1996). (b) A. Razavi, G. Debras, PCT Int. Appl. 96/35729 (1996).
[213] T. Tsutsui, K. Yoshitsugu, M. Ohgizawa, J. Imuta, T. Matsumoto, Eur. Pat. Appl. 697,419 (1996).
[214] J.L. Brinen, PCT Int. Appl. 96/28749 (1996).
[215] T. Tsutsui, K. Yoshitsugu, K. Yamamoto, K. Doi, N. Suzuki, Eur. Pat. Appl. 723,976 (1996).
[216] P. Brant, PCT Int. Appl. 96/34020 (1996).
[217] J.R. Griffin, M.E. Muhle, G.T. Renola, D.L. Litteer, P. Brant, US Patent 5,763,543 (1998), based on PCT Int. Appl. 96/08520 (1996).
[218] E.E. Poirot, V.R. Sagar, S.K. Jackson, US Patent 5,712,353 (1998), based on PCT Int. Appl. 96/08521 (1996).
[219] M.E. Muhle, A.K. Agapiou, G.T. Renola, US Patent 5,672,666 (1997), based on PCT Int. Appl. 96/39450 (1996).
[220] G.G. Hlatky, D.J. Upton, Macromolecules 29 (1996) 8019.
[221] (a) J. Lynch, D. Fischer, F. Langhauser, H.-H. Görtz, J. Kerth, G. Schweier, Eur. Pat. Appl. 700,934 (1996). (b) D. Fischer, F. Langhauser, J. Kerth, G. Schweier, J. Lynch, H.-H. Görtz, Eur. Pat. Appl. 700,935 (1996).
[222] D.G. Ward, PCT Int. Appl. 96/40796 (1996).
[223] O. Lhost, N. Zandona, Eur. Pat. Appl. 733,650 (1996).
[224] J.F. Walzer, Jr., US Patent 5,643,847 (1997).
[225] D.G. Ward, E.M. Carnahan, PCT Int. Appl. 96/23005 (1996).
[226] S. Hinokuma, S. Miyake, M. Ono, S. Inazawa, Eur. Pat. Appl. 775,707 (1997), based on PCT Int. Appl. 96/41808 (1996).
[227] G.B. Jacobsen, P. Wijkens, J. Jastrzebski, G. Van Koten, PCT Int. Appl. 96/28480 (1996).
[228] T. Kaneko, M. Sato, Eur. Pat. Appl. 727,433 (1996).
[229] R.I. Mink, T.E. Nowlin, P.P. Shirodkar, S.D. Schregenberger, G.O. Tsien, US Patent 5,614,456 (1997), based on PCT Int. Appl. 96/14154 (1996).
[230] M. Sacchetti, S. Pasquali, G. Govoni, US Patent 5,691,264, based on PCT Int. Appl. 96/01855 (1996).
[231] T.M. Pettijohn, US Patent 5,622,906 (1997), based on Eur. Pat. Appl. 705,848 (1996).
[232] M. Chang, US Patent 5,529,965 (1996).
[233] E.S. Shamshoum, D.J. Rauscher, C.G. Bauch, US Patent 5,767,031 (1998), based on Eur. Pat. Appl. 747,402 (1996).
[234] T.E. Nowlin, S.D. Schregenberger, P.P. Shirodkar, G.O. Tsien, PCT Int. Appl. 96/07478 (1996).
[235] R.I. Mink, T.E. Nowlin, P.P. Shirodkar, S.D. Schregenberger, G.O. Tsien, US Patent 5,525,678 (1996).
[236] G. Govoni, M. Sacchetti, S. Pasquale, US Patent 5,589,549 (1996).
[237] K. Bujadoux, B. Leprevost, X. Olonde, E. Adisson, S. Agabossou, Eur. Pat. Appl. 720,989 (1996).
[238] A.E. Hamielec, J.B.P. Soares, Prog. Polym. Sci. 21 (1996) 651.

[239] M. Eskelinen, J.V. Seppälä, Eur. Polym. J. 32 (1996) 331.

[240] R.S. Mauler, G.B. Galland, R.B. Scipioni, R. Quijada, Polym. Bull. 37 (1996) 469.

[241] M. Lahti, J. Koivumäki, J.V. Seppälä, Angew. Makromol. Chem. 236 (1996) 139.

[242] M. Lahti, J. Koivumäki, J.V. Seppälä, Angew. Makromol. Chem. 236 (1996) 155.

[243] H. Hokkanen, H. Salminen, K. Kallio, H. Knuuttila, A. Palmroos, PCT Int. Appl. 96/34895 (1996).

[244] D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 197 (1996) 855.

[245] R. Fusco, L. Longo, L. Gila, F. Cambisi, Eur. Pat. Appl. 741,146 (1996).