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Single-site catalysts for olefin polymerization: Annual review for 1997

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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-ethylene (1-indenyl) ligand; $Et(H_4\text{-}Ind)_2$, 1,2-ethylenebis(tetrahydroindenyl) ligand; Flu, fluorenyl; MAO, methylalumoxane.

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Abstract

Papers, patents, and published patent applications from 1997 on olefin polymerization by single-site catalysts and processes in which they are used are reviewed. Included are disclosures on cocatalyst preparation, and the copolymerization of α-olefins and carbon monoxide by metal complexes.

Keywords: Metallocene catalysts; Single-site; Olefin polymerization; Cyclopentadienyl complexes; Carbon monoxide copolymers

1. Introduction

This review covers research in olefin polymerization by single-site catalysts published in 1997. The scope of this survey will be somewhat broader than that of the 1996 review [1], taking in non-metallocene single-site catalysts. Therefore, the four classes of single-site catalysts to be reviewed are:

- mono- and bis(cyclopentadienyl) catalysts;
- catalysts with isolobal equivalents to cyclopentadienyl ligands;
- catalysts with non-cyclopentadienyl anionic ancillary ligands;
- catalysts with neutral ancillary ligands.

The function of the ancillary ligand in all these metal complexes is the same: to maintain a single type of active polymerizing site. Not only are the polymers from single-site catalysts are notable for the narrowness of their molecular weight and composition distributions, but the catalyst precursors and active catalyst species are often characterizable to a far greater extent than conventional Ziegler–Natta catalysts.

Included in this review will be certain disclosures concerning cocatalyst preparation and use. Polymer properties and uses will not be covered.

Open literature publications and basic patent cases from 1997 were taken from searches of a number of online databases including Chemical Abstracts, Current Contents, Derwent World Patent Index, and U.S. Patents Fulltext. Whenever a published patent application has subsequently issued as a U.S. patent, the U.S. 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. Japanese

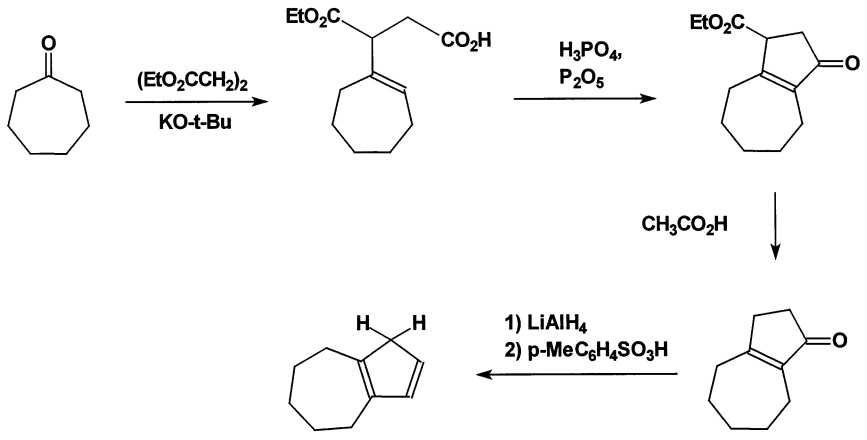

Fig. 1. Preparation of fused-ring cyclopentadienones from cyclic ketones.

Kokai applications, which are rarely filed outside Japan, will be addressed to the extent that the abstract gives a clear picture of the unique aspect of the invention.[1]

The reader's attention is drawn to a number of general review articles on olefin polymerization by single-site catalysts which appeared in 1997 [2].

2. Preparations 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.

Polyalkylated cyclopentadienes are produced from the reaction of cyclopentadiene and an excess of alkyl halides and NaOH. The polyalkylcyclopentadienes may bear geminal substituents. These can be converted to non-geminal cyclopentadienes by reaction with potassium [3]. Thus tetraethylcyclopentadiene containing 6%

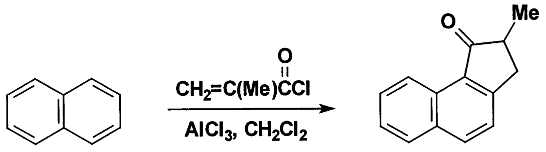

Fig. 2. Synthesis of 2-methylbenz[e]indan-1-one.

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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 and interpretations expressed in this review are solely those of the author.

geminal substitution is converted to triethylcyclopentadiene after refluxing with metallic potassium in dimethoxyethane.

Cyclopentenones and indanones are important starting materials in the formation of substituted cyclopentadienides. 2,5-Hexanedione reacts with NaOH in a two-phase (water/toluene) reaction mixture to form 3-methylcyclopent-2-ene-1-one in 74% yield [4].

Cyclic ketones are condensed with diesters to produce fused ring cyclopentadienes in a multi-step reaction (Fig. 1) [5].

Reacting naphthalene, methacrolyl chloride, and $AlCl_3$ in CH_2Cl_2 yields 2-methylbenz[e]indan-1-one (Fig. 2) [6]. The indanone is allowed to react with $NaBH_4$ to form the indanol, which is not isolated but immediately dehydrated with *p*-toluenesulfonic acid to afford 2-methylbenz[e]indene. Deprotonation and reaction with Me_2SiCl_2 forms the bridged ligand. This is deprotonated and $ZrCl_4$·TMEDA is added to form *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ with little *meso* byproduct [7]. Indanones can also be converted to indenes by hydrogenating over solid acid catalysts like zinc oxide [8]. An active catalyst can be prepared in situ by allowing zirconium alkoxides to react with indene or 1,2-bis(indene)ethane in the presence of triisobutylaluminum and methylalumoxane (MAO) [9].

Metallocene complexes for isospecific α-olefin polymerization are overwhelmingly *ansa*-bis(indenyl) metal complexes. Syntheses of these complexes frequently produce undesirable *meso* isomer, which forms atactic polymers. A desirable preparation is one which enhances the yield of the *rac* isomer and minimize formation of the *meso* isomer. The reaction of lithium 2-methylbenz[e]indenide with the ditosylate of 2,3-butanediol affords a chiral ligand set which can be deprotonated and metalated to give an isospecific catalyst precursor (Fig. 3) [10].

$Zr(NMe_2)_4$ reacts with $Me_2E(H\text{–}Ind)_2$ ($E = C$, Si) to form the *ansa* metallocenes $Me_2E(Ind)_2Zr(NMe_2)_2$ in 50% yield (*rac*/*meso* = 9:1) [11]; this can be activated for propylene polymerization by MAO or $AlMe_3/[Ct][B(C_6F_5)_4]$ [12]. However, the

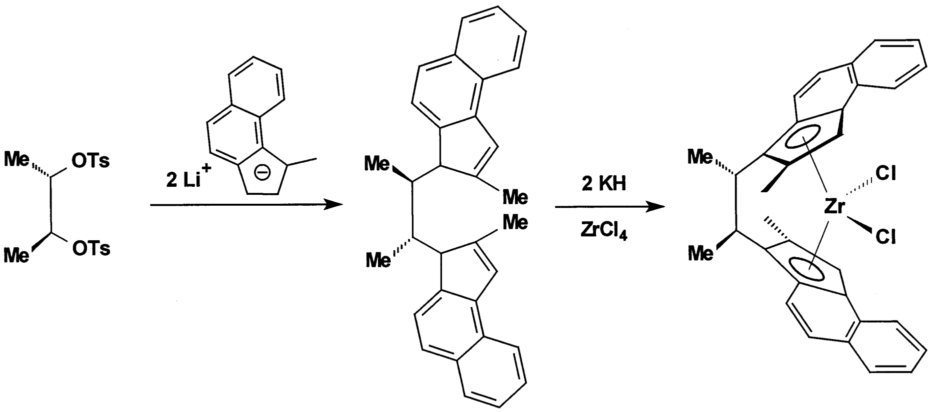


Fig. 3. Synthesis of 2,3-diindenylbutane zirconium dichlorides.

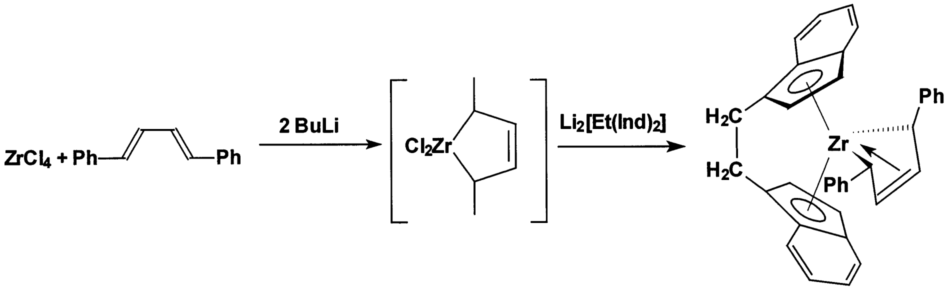


Fig. 4. Synthesis of metallocene diene complexes.

reaction of $Me_2Si(Ind–H)_2$ with $Hf(NMe_2)_4$ produces *rac*-$Me_2Si(Ind)_2Hf(NMe_2)_2$ in lower yield (20% isolated) [13]. Mixed ring *ansa* metallocenes are accessible through the reaction of $Me_2C(H–Cp)(H–Ind)$ with $Zr(NMe_2)_4$ [14]. The distannylated complexes $(\mu\text{-A})(Ind\text{-}SnMe_3)_2$ ($A = Me_2C$, Me_2Si, $1,2\text{-}C_2H_4$) reacts with $ZrCl_4$ or $HfCl_4$ to form equal amounts of the *rac* and *meso* isomers of the *ansa* metallocenes $(\mu\text{-A})(Ind)_2MCl_2$ [15].

The *meso* and *rac* stereoisomers of $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ can be chromatographically separated by passing through a column of porous carbon [16]. The *meso* isomer of $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuCp)_2ZrCl_2$ is converted to the *rac* isomer when irradiated by an Hg lamp in the presence of dilithium *R*-(+)-1,1′-bi-2-naphtholate [17]. Mixtures of *rac* and *meso*-$Me_2Si(2\text{-}MeInd)_2ZrCl_2$ containing LiCl and $ZrCl_4$ contaminants are purified by heating in THF (5–15 ml g^{-1} metallocene) [18] or suspending in isobutanol [19] and filtering to leave the *rac* isomer. The *R* and *S* enantiomers of *rac*-$Et(Ind)_2MCl_2$ (M = Zr, Hf) can be resolved by conversion of the dichloride to the 2,2′-biphenolate and chromatographing with cellulose tris(3,5-dimethylphenylcarbamate) as the stationary phase [20].

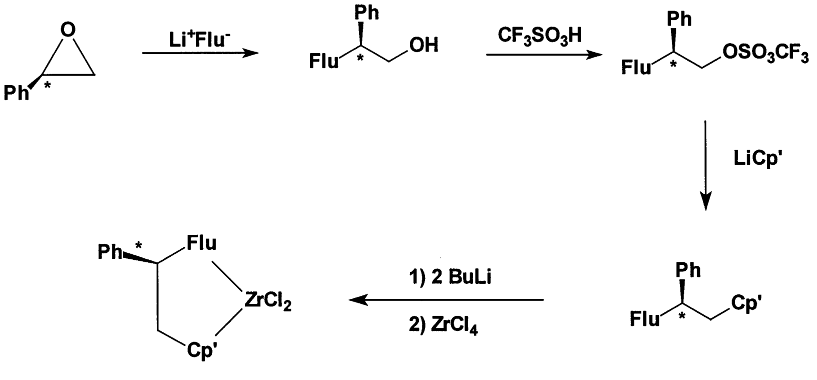


Fig. 5. Synthesis of chiral-bridged *ansa* metallocenes.

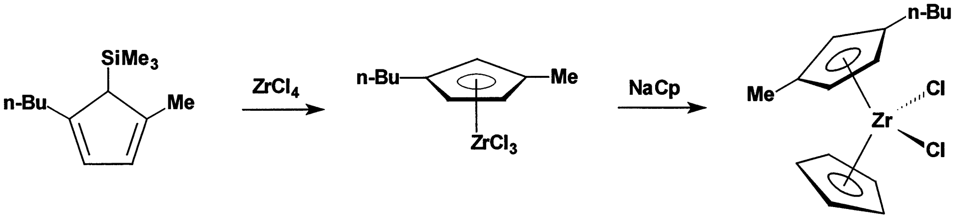


Fig. 6. Synthesis of mixed-ring metallocene complexes.

Bis(cyclopentadienyl) metal diene complexes, useful as procatalysts with $B(C_6F_5)_3$, can be prepared by allowing MCl_4 to react with the diene in the presence of butyllithium to generate an unisolated diene dichloride intermediate. This reacts with cyclopentadienyl anions to form the metallocene diene product (Fig. 4) [21]. Me_2ZrCl_2 (from $ZrCl_4$ and MeLi) can also function as the intermediate for producing (μ-A)$(Ind)_2ZrMe_2$ complexes (A = 1,2-xylyl, 1,4-but-2-enyl, 1,2-ethyl, and Me_2Si) [22].

Rieger and co-workers prepared enantiomerically pure *ansa*-zirconcenes and hafnocenes by reacting (*R*)-epoxystyrene with fluorenyllithium, converting the alcohol to the trifluoromethanesulfonate, then reacting with fluorenyl- or indenyllithium (Fig. 5) [23]. The metalated products can be hydrogenated to 1,2-$CH_2CHPh(H_4{-}Ind)(H_8{-}Flu)ZrCl_2$ or 1,2-$CH_2CHPh(H_8{-}Flu)_2ZrCl_2$.

Mixed ring zirconocenes have been prepared through the reaction of the substituted trimethylsilylcyclopentadiene with $ZrCl_4$ and subsequently allowing the $Cp'ZrCl_3$ intermediate to react with NaCp′ (Fig. 6) [24].

Cyclopentadienyltitanium trichlorides are converted to trialkoxides useful in syndiospecific styrene polymerization by reaction with concentrated alcoholic

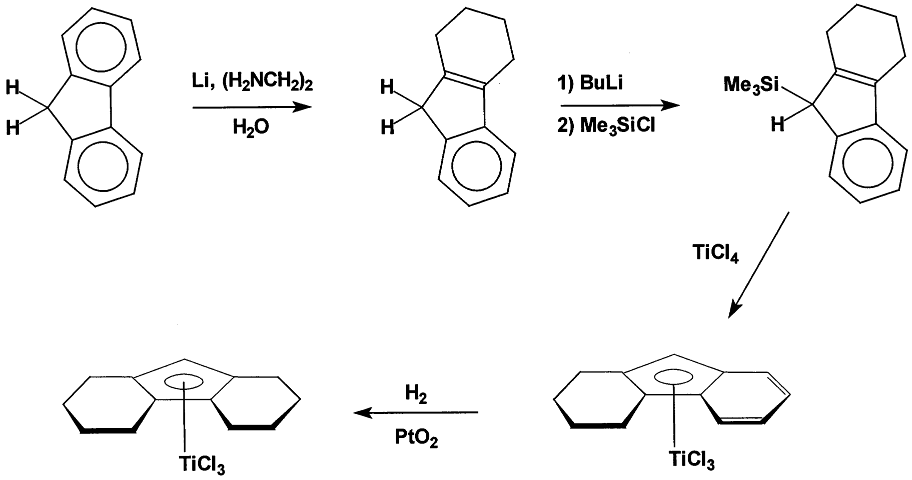


Fig. 7. Synthesis of octahydrofluorenyltitanium trichloride.

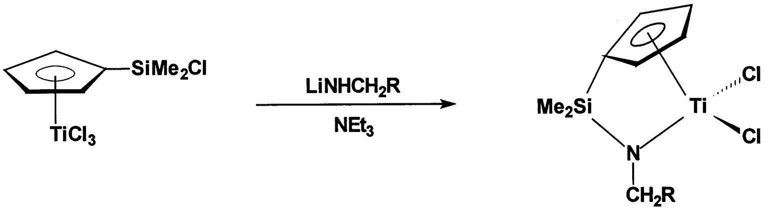


Fig. 8. Synthesis of bridged mono(cyclopentadienyl)titanium complexes.

sodium alkoxides; yields are higher and voluminous precipitates formed in the reaction of the metal halide with alcohols in the presence of an amine are avoided [25]. Octahydrofluorenyltitanium trichloride is produced by synthesizing tetrahydrofluorenyltitanium trichloride, then hydrogenating over PtO_2 (Fig. 7) [26]. $Cp^*Ti(OMe)_3$ is reduced to $Cp^*Ti(OMe)_2$ by reaction with *t*-BuLi followed by a quenching agent like Me_3SiCl [27].

A unique method of preparing $Me_2Si(Cp)(N{-}CH_2R)TiCl_2$ complexes (R = *i*-Pr, Ph, 2,4-$C_6H_3F_2$), developed by Okuda and co-workers, uses the reaction of $(ClMe_2SiCp)TiCl_3$ with the lithium salt of the amine in the presence of triethylamine (Fig. 8); an excess of ammonium salt by-product is avoided [28]. In contrast, a bridge-breaking reaction occurs when dimethylsilyl-bridged bis(indenyl) zirconocenes are converted to $(Ind)(ClMe_2SiInd)ZrCl_2$ complexes by reaction with HCl in chloroform or CH_2Cl_2 (Fig. 9) [29].

3. Ring substituents

Changes in the ring substituents of metallocene catalysts can have a profound influence on activity, molecular weight, comonomer incorporation, and stereospecificity. Hydrocarbyl (alkyl and aryl) and silahydrocarbyl (e.g. $-SiMe_3$) groups are largely preferred. Cp'_2ZrCl_2 complexes with long-chain substituents (e.g. $(Me(CH_2)_{11}C_5H_4)_2ZrCl_2$) have higher activities than Cp_2ZrCl_2, attributed to the higher solubility of the metallocene in aliphatic diluents [30]. Other classes of cyclopentadienyl substituents have also been explored.

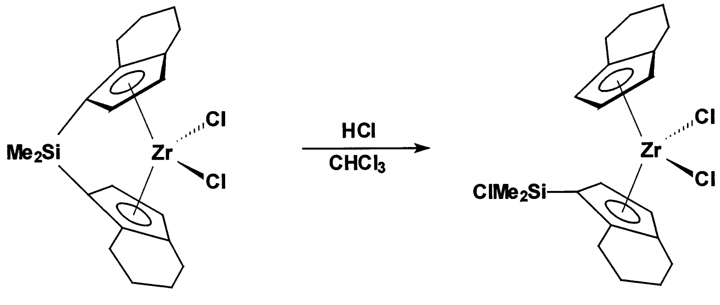
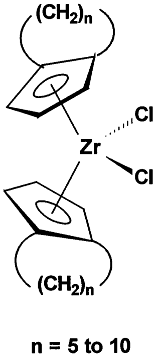


Fig. 9. Bridge-breaking reaction in *ansa* metallocenes.

Metallocenes with large fused saturated ring substituents like bis(4,5,6,7,8-pentahydro-azulenyl)zirconium dichloride (**1**) were produced from the lithium cyclopentadienides [5] and $ZrCl_4$; these were used with MAO to copolymerize ethylene and propylene [31].



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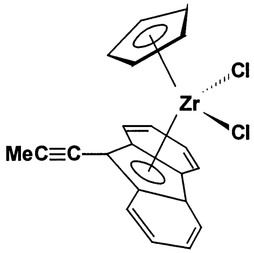
The alkyne group in the complex Cp(9-(prop-2-ynyl)Flu)$ZrCl_2$ (**2**) was used to enhance adsorption of the metallocene on a silica support [32].



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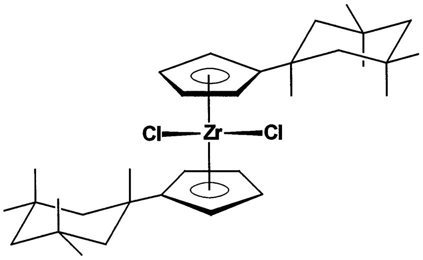
The sterically hindered bis(1,3,3,5,5-pentamethylcyclohexylcyclopentadienyl) zirconium dichloride complex (**3**)—produced from reacting MeLi and the condensation product of 3,3,5,5-tetramethylcyclohexanone with cyclopentadiene—polymerizes ethylene with good activity in the presence of MAO; low MW atactic polypropylene oligomers are also produced [33].



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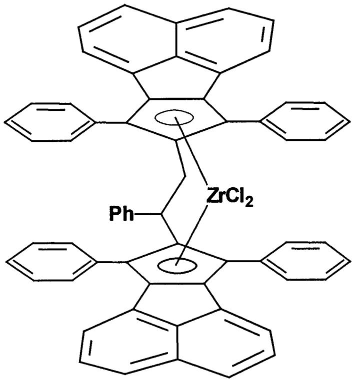
The sterically demanding 7,9-diphenylcyclopenta[*a*]acenaphthadienyl ligand has been used to prepare zirconocenes as bridged (with $-CH(Ph)CH_2-$, like **4** and **5**) and unbridged complexes [34].



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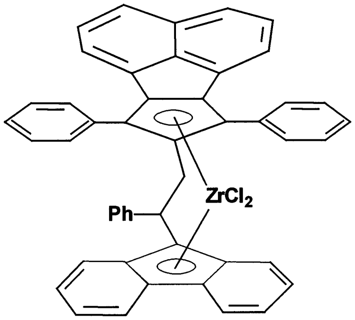

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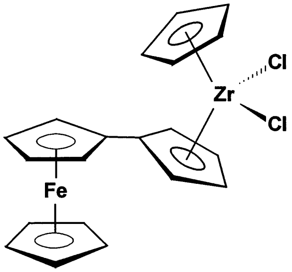
Ethylene is polymerized in the presence of MAO, but, surprisingly for so sterically constricted a catalyst site, propylene is also polymerized to atactic products.

Ferrocenyl-substituted cyclpentadienides were allowed to react with $CpZrCl_3$ to produce zirconocenes such as **6** with dimethylsilylferrocenyl ring substituents. These were used with $Al(i\text{-}Bu)_3-[Ph_3C][B(C_6F_5)_4]$ to cyclopolymerize 1,5-hexadiene to polymer with a high *trans* content [35].



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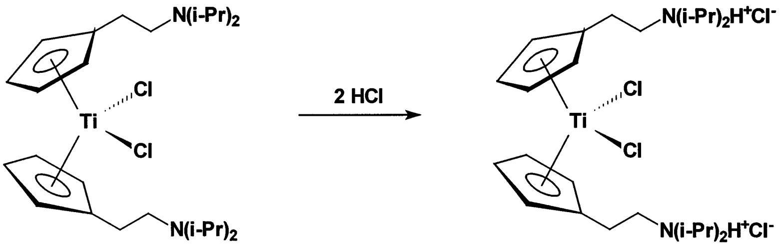
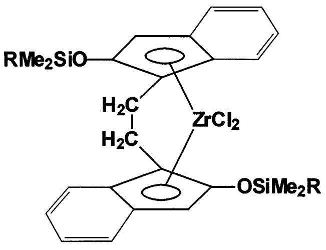


Fig. 10. Formation of dicationic titanocene dichloride complex.

Metallocene complexes with substituents containing nitrogen or oxygen atoms connected directly to the 5-membered ring are not as common as the hydrocarbyl-substituted complexes, but their numbers are increasing. Catalysts based on alkyldimethylsiloxyindenes such as **7** (R = *t*-Bu, *t*-hexyl, cyclohexyl) have been synthesized and used in ethylene and propylene polymerizations [36].



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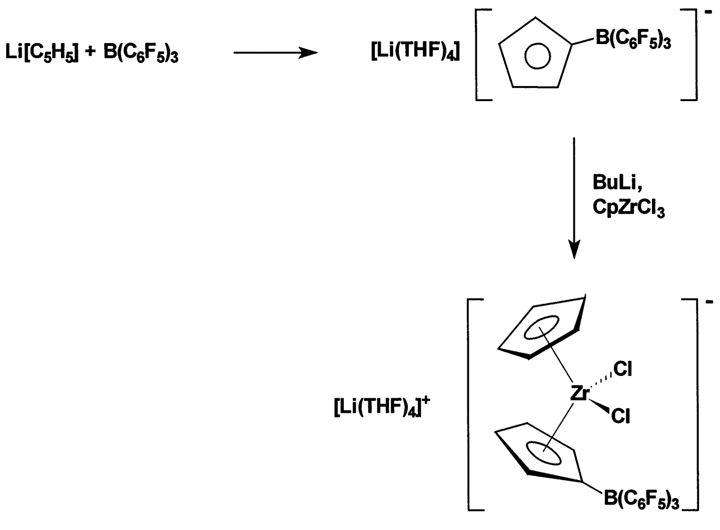


Fig. 11. Synthesis of anionic zirconocene complex.

The indenyl-based catalysts show high activities at quite low MAO ratios (Al:M = 100–300:1) but the tetrahydroindenyl derivatives are far less active.

Metallocenes bearing polar groups at more remote locations have also been synthesized. Fluorine-containing zirconocenes like $(3,5\text{-}(CF_3)_2PhCp)_2ZrCl_2$ cocatalyzed by MAO are claimed to polymerize ethylene to higher molecular weight polymer than Cp_2ZrCl_2 [37].

$((i\text{-}Pr)_2NCH_2CH_2Cp)_2TiCl_2$ is protonated by HCl to form the dicationic dichloride complex, which, in the presence of MAO, polymerizes ethylene (Fig. 10) [38]. The neutral complex can also be used as a catalyst in the presence of MAO; by adding HCl to the polyethylene formed, the protonated complex can be extracted and recycled [39].

The Lewis-acidic $B(C_6F_5)_3$ group was used as a ring substituent by the reaction of $B(C_6F_5)_3$ with lithium cyclopentadienide, forming $Li[C_5H_5\text{–}B(C_6F_5)_3]$. Deprotonation with butyllithium in THF affords the dianion, which can react with $Cp'MCl_3$ to give the anionic bis(cyclopentadienyl) complex (Fig. 11) [40]. When contacted with MAO or $Al(i\text{-}Bu)_3\text{–}[Ph_3C][B(C_6F_5)_4]$, these compounds function as olefin polymerization catalysts.

4. Bridging groups

Interannular bridges in bis(cyclopentadienyl) metal complexes serve to fix the rings in a particular orientation; the induced rigidity is especially important in stereospecific α-olefin polymerization. They also affect the performance of the catalyst by changing the ring-metal-ring angle, thereby opening the active site to olefins bulkier than ethylene.

1,2-Ethylene bridges and Me_2Si units are the most widely used bridging groups, but some variations in these two functionalities have been reported in 1997. Introduction of a vinyl group into the R_2Si bridge was claimed to lead to an enhanced fraction of *rac* isomer in the synthesis of the $R_2Si(2,4\text{-}Me_2Cp)_2ZrCl_2$; the (vinyl)(Me)Si derivative has catalyst activity and isotacticity higher than the Me_2Si complex [41]. $(Me_3Si)(R)Si$-bridged zirconocenes ($R = Me$, Me_3Si) polymerize ethylene and higher α-olefins in the presence of MAO, though no comparative examples were provided to determine any improvements in catalyst performance [42]. The disiloxane-bridged complexes $(Me_2Si\text{–}O\text{–}SiMe_2)(Cp')_2ZrCl_2$ ($Cp' = Ind$, $H_4\text{–}Ind$, Cp, *t*-BuCp) polymerize ethylene most effectively between 40–60°C; the *rac* isomers are somewhat more active and produce polyethylene of slightly higher molecular weight than do the *meso* isomers, with the effect more pronounced at 20°C and below [43].

1,1-Difluorenylalkenyl and 1,2-dialkyl-1,2-difluorenyl zirconium and hafnium complexes are prepared by addition of butyllithium to fulvene or difulvene derivatives of fluorene (Fig. 12) [44]. The two-carbon bridged complexes are more active in ethylene polymerization than the one-carbon compounds and the zirconocenes are 10–100 times more active than the hafnocenes. Bis(fluorenyl)zirconium and –hafnium dichlorides with $\text{–}CH_2SiMe_2\text{–}$ and $\text{–}Si_2Me_4\text{–}$ bridges were tested in

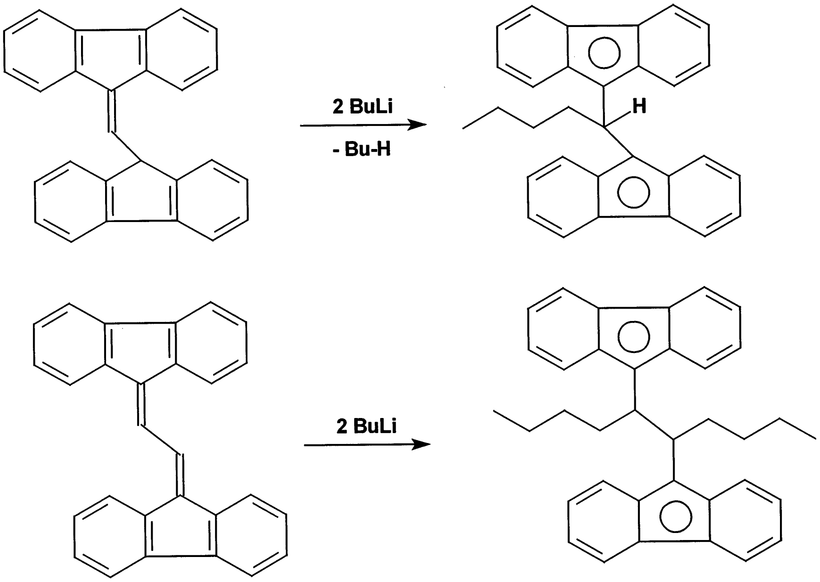


Fig. 12. Synthesis of 1,2-ethylenebis(fluorenyl) dianions.

ethylene polymerizations; the carbon-containing complexes were considerably more active than the disilyl-bridged complexes [45].

The *trans*-1,2-alkylene-bridged bis(indenyl) and bis(tetrahydroindenyl) complexes of titanium, zirconium, and hafnium were synthesized with five to eight membered rings bridging the indenyl ligands (Fig. 13) [46]. Both *rac*-like (staggered indenyl groups) and *meso*-like (eclipsing indenyl groups) isomers were isolated. The former were active in the isospecific polymerization of propylene, but the latter were virtually inactive, attributed to steric crowding of the active site.

New bridging moieties reported in 1997 include the α,α′-*o*-xylyl group, used to bridge two indenyl ligands as in **8**.

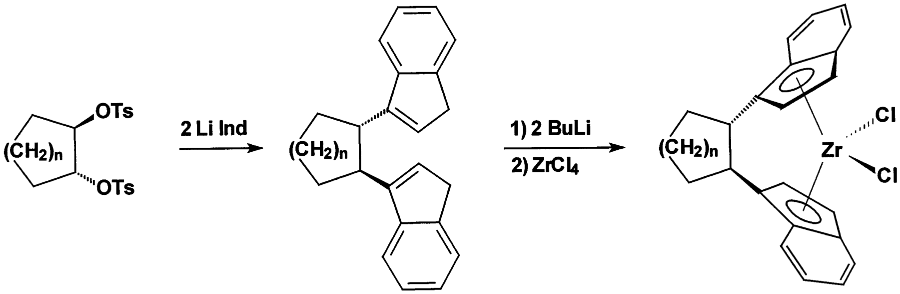


Fig. 13. Synthesis of *trans*-1,2-cycloalkylenebis(indenyl)zirconium dichlorides

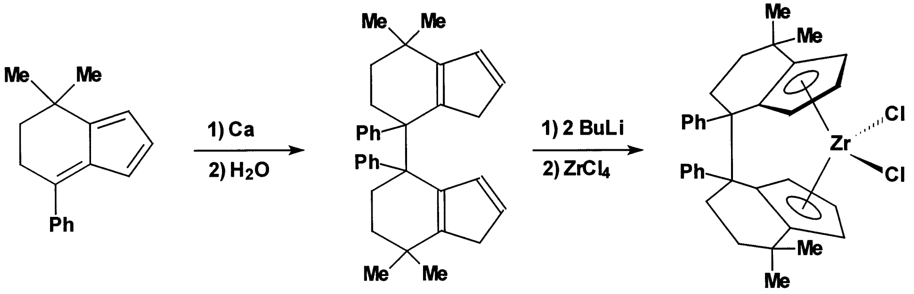
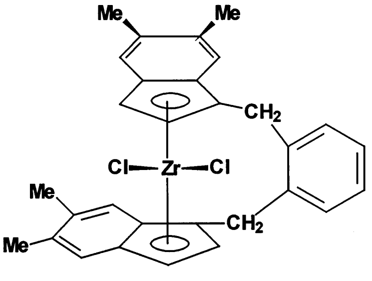


Fig. 14. Synthesis of *ansa* bis(indenyl) zirconium dichloride.



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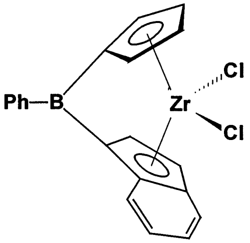
As can be seen the distortion of the C_2 symmetry makes these complexes aspecific in propylene polymerization, but their high temperature performance makes them valuable in ethylene-α-olefin copolymerizations [47].

Calcium couples the bicyclic fulvene compound to make a substituted bis(tetrahydroindenyl) ligand which can be deprotonated and metalated to form the zirconocene complex (Fig. 14) [48]. In the presence of MAO (Al:Zr = 1500–43 000), this compound polymerizes propylene to moderately isotactic polypropylene.

Boron-bridged zirconocene complexes like **9** [49] and **10** [50] represent a new class of *ansa* metallocenes with electron-deficient bridges. In the presence of MAO, **10** is unreactive toward ethylene when $L = Me_2S$, but a more stable, polymerization-active catalyst is formed when $L = PMe_3$.



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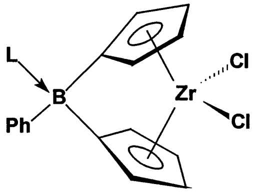

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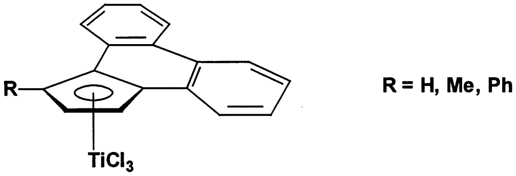
A double-bridged zirconocene $(Me_2Si)_2(C_5H_3)_2ZrCl_2$ was synthesized and used in the copolymerization of ethylene and styrene; the molecular of the copolymer (MW = 12 000) appears to be low [51].

5. Mono(cyclopentadienyl) complexes

Two classes of mono(cyclopentadienyl)metal complexes, especially those of titanium, currently command much research interest. The unbridged $Cp'TiX_3$ compounds find use as catalysts for the syndiospecific polymerization of styrene, while bridged mono(cyclopentadienyl) compounds like $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$ are notable for producing very- to ultra-low-density ethylene copolymers which are claimed to have enhanced processibility.

Brintzinger and coworkers prepared and tested the 2-substituted cyclopenta[*l*]phenanthrene titanium dichoride complexes (**11**) in styrene polymerizations [52].



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The 2-phenyl derivative exhibits higher activities and polymer molecular weights than do the unsubstituted or methyl-substituted complexes and the catalyst syndiospecificity remains almost unchanged between 50 and 100°C.

$(Ind)TiCl_3$ complexes variously substituted on the indenyl ring were examined in syndiospecific styrene polymerization [53]. Electron-donating alkyl groups improve catalyst activity so long as they do not impose sterically on the active site. Therefore, $(1\text{-}MeInd)TiCl_3$ is a more active and syndiospecific catalyst than $(Ind)TiCl_3$ or $(1\text{-}i\text{-}PrInd)TiCl_3$.

Reacting $Et_2O{\cdot}FB(C_6F_5)_2$ with Cp′Li give $Cp'{-}B(C_6F_5)_2$ (Cp′ = Ind, Flu, Me_3SiCp). When $Ind{-}B(C_6F_5)_2$ is allowed to react with $Zr(NMe_2)_4$, a pentafluorophenyl group is lost and $(C_9H_6B(C_6F_5)(NMe_2))Zr(NMe_2)_3$ (**12**) is formed,

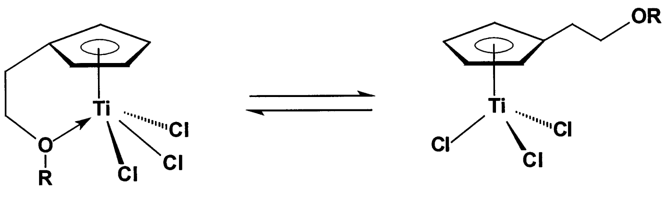
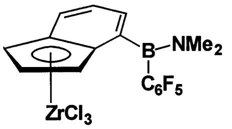


Fig. 15. Equilibrium between bridged and unbridged mono(cyclopentadienyl)titanium complexes.

which can be converted to the trichloride on reaction with Me_3SiCl. When $TiCl_4$ is allowed to react with $Me_3SiCp{-}B(C_6F_5)_2$, the mono(cyclopentadienyl)titanium complex (**13**) is formed.



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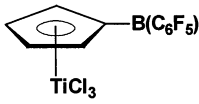

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In the presence of $AlEt_3$, both **12** and **13** polymerize ethylene, unlike $(Ind)ZrCl_3$ or $CpTiCl_3$ [54].

Mono(cyclopentadienyl) complexes with pendant ether substituent groups do not exhibit activity in the polymerization of styrene and only modest activity in ethylene polymerization [55]; butadiene is polymerized to a fairly stereospecific homopolymer [56]. The relatively poor catalyst activity has been attributed to coordination of the ether group with MAO cocatalyst [55a] or to poor catalyst solubility in the case of $[\eta^5{:}\eta^1\text{-}(MeOCH_2CH_2Cp)ZrCl_2(\mu\text{-}Cl)]_2$ [55b]. Temperature-dependent NMR of $(ROCH_2CH_2Cp)TiCl_3$ indicates that about 30% of the complex exists as the ether-coordinated conformer when $R = Me$ (Fig. 15), but coordination is reduced when R is the larger menthyl or fenchyl groups [55b].

The amine group in $(C_5Me_4CH_2CH_2NMe_2)TiCl_3$ can be protonated with HCl and then allowed to react with $Li[B(C_6F_5)_4]$ to create a mono(cyclopentadienyl) titanium complex with its own internal activator; reaction of this complex with MAO or $AlEt_3$ generates an active catalyst species (Fig. 16) [57].

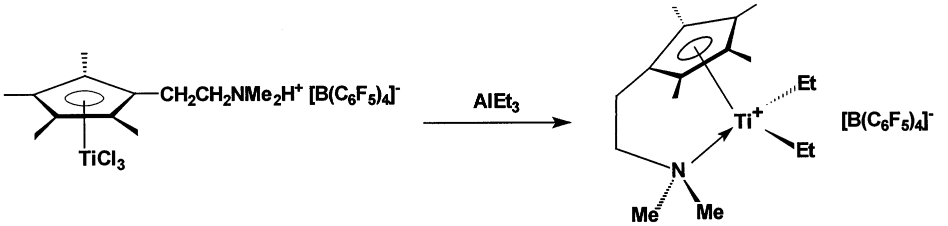
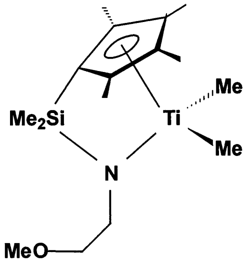


Fig. 16. Generation of active catalyst from a protonated (aminocyclopentadienyl)titanium complex.

New ‘constrained-geometry’ catalyst precursors were reported in 1997. While the tetramethylcyclopentadienyl-based complex $Me_2Si(C_5Me_4)(N{-}R)TiCl_2$ is the most widely known, the tetraethyl- and tetrapropylcyclopentadienyl derivatives with silane- and germane bridges were also synthesized and tested in ethylene-α-olefin polymerization [58]. Less substituted cyclopentadienyl complexes (e.g. $Me_2Si(C_5H(2\text{-pentyl})_4)(N\text{-}t\text{-}Bu)TiCl_2$ were similarly prepared and used as catalysts [59].

Polymerization of ethylene by indenyl-based complexes variously substituted with alkyl groups, such as $Me_2Si(2,3,4,6\text{-}Me_4Ind)(N\text{-}i\text{-}Pr)TiMe_2$, affords polymer of higher molecular weight than that obtained from the tetramethylcyclopentadienyl derivative [60]. Changes in the group attached to nitrogen can have an effect on catalyst performance as well: the 2-methoxyethylamido complex **14** has superior productivity and comonomer response than the *t*-butyl derivative in high-temperature, high-pressure polymerizations (1500 bar, 230°C) [61].



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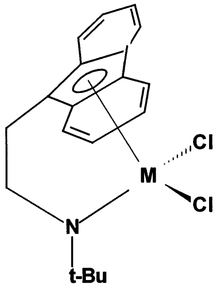
‘Constrained-geometry’ catalysts with alkylene bridges are represented by the 1,2-ethylene-bridged fluorenyl complexes of zirconium and hafnium (**15**) and 1,2-$Et(Cp)(N\text{-}t\text{-}Bu)Ti(CH_2Ph)_2$, which polymerize ethylene in the presence of MAO [62].



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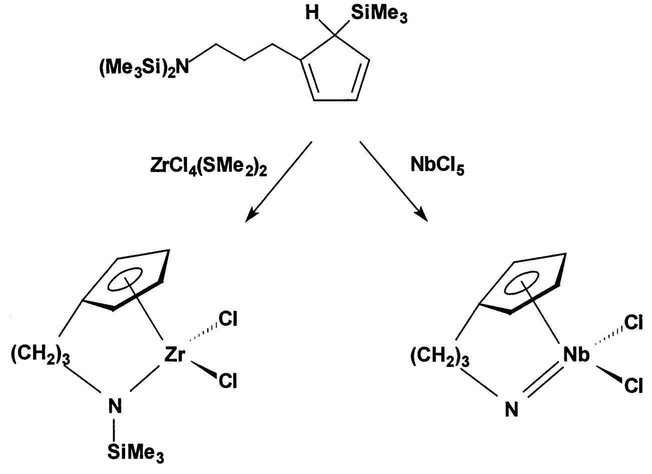
Tri(methylene)-bridged complexes of zirconium (**16**) and niobium (**17**) are prepared by reaction of the trimethylsilylated cyclopentadiene derivative with $ZrCl_4(SMe_2)_2$ [63] or $NbCl_5$ [64] (Fig. 17).

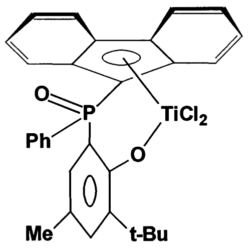


16 **17**

Fig. 17. Synthesis of *ansa* mono(cyclopentadienyl) amide zirconium and niobium complexes.

In the presence of MAO, the zirconium compound is an active catalyst for ethylene or propylene polymerization, but the niobium complex is inactive, attributed to an unfavorable orbital arrangement.

Investigators at Sumitomo have developed a series of *ansa*-mono(cyclopentadienyl) titanium complexes in which a 3-*t*-butyl-5-methyl-2-phenoxide group serves as the heteroatom-bearing moiety. Not only are 1,2-ethylene [65] and Me_2Si [66] groups used as bridging groups but also unusual functionalities such as sulfur and phenylphosphine oxide, as in **18** [67].



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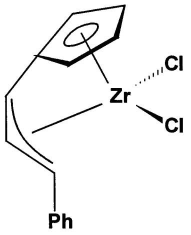
Unusual as well is the bridging allyl group claimed for **19**, which functions as a catalyst for the copolymerization of ethylene and 1-hexene when MAO is used as the cocatalyst [68].



19

The ligand is prepared by allowing lithium cyclopentadiene to react with cinnamyl chloride; double deprotonation of the product and metalation with $ZrCl_4$ affords the complex.

The family of trivalent mono(cyclopentadienyl) titanium amide complexes first reported by DSM in 1996 was greatly expanded in 1997. A large number of new derivatives was disclosed, with differing ring substituents, bridges, and heteroatom donors (Table 1). The double-bridged complex $(Et)_2(C_5(i\text{-Pr})_3)(NMe_2)_2TiCl_2$ included in this class of procatalysts copolymerizes ethylene and propylene in the presence of MAO. Copolymers with both narrow [69] and broad [70] molecular weight distributions can be prepared from these catalysts; the reasons for this difference were not disclosed, but the former polymers appear to have been made in a continuous process while a batch process was used for the latter.

6. Non-cyclopentadienyl ligands

Single-site catalysts depend on the presence of a polymerization-stable ligand set to prevent formation of secondary catalytic species; much effort has been spent on discovering and developing new ancillary ligands. The other ligands which react with the cocatalyst in forming the active catalyst site have not been ignored by researchers and some surprising findings were reported in 1997.

Kaminsky and co-workers and investigators at Asahi have found that fluorinated half-metallocene complexes such as $CpTiF_3$ and Cp^*TiF_3 exhibit higher catalyst activities at higher temperatures than their trichloride analogues [71]. Polymer molecular weights are significantly greater as well: Cp^*TiF_3 affords syndiotactic polystyrene (s-PS) with a molecular weight of 660 000 at 50°C versus 169 000 for Cp^*TiCl_3 under similar conditions.

The use of phenoxides as reactive groups in $Cp_2ZrCl(OAr)/MAO$ complexes (OAr = 2,6-di-*t*-butylphenoxide, 2,6-di-isopropylphenoxide) give catalysts with higher activity in ethylene polymerization than the Cp_2ZrCl_2 counterpart, though the polymer properties do no appear to be affected [72]. Either the greater solubility of the phenoxide complex in hydrocarbons or the rate of activation was held responsible for the rate increase. The mono(cyclopentadienyl) zirconium complex $Cp^*ZrCl(O\text{-}2\text{-}Me_2NC_6H_4)_2$ was allowed to react with MAO to give a catalyst for the production of high molecular weight polyethylene [73] and $Cp_2Zr(OMe)_2$–MAO was examined as a catalyst in ethylene-1-butene copolymerizations in a hexane diluent [74]. Propylene is polymerized at 0°C by the trifluoromethanesulfonate complex $Cp_2TiMe(O_3SCF_3)$ in combination with MAO [75].

Table 1
$Cp'A(Y)Ti^{(III)}Cl_2$ complexes

Cp'	A	Y	Ref.
$C_5H_2(c\text{-}C_6H_{11})_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,b,e
$C_5H_2(2\text{-pentyl})_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,c,e
$C_5H(i\text{-}Pr)_3$	$1,2\text{-}CH_2CH_2$	NMe_2	a,e,d
$C_5H_2(2\text{-pentyl})_2$	$1,2\text{-}CH_2CH_2$	$N(n\text{-}Bu)_2$	a,c,e
$C_5H_2(2\text{-butyl})_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,c,e
$C_5H(2\text{-butyl})_3$	$1,2\text{-}CH_2CH_2$	NMe_2	a,c,e
$C_5H(c\text{-}C_6H_{11})(i\text{-}Pr)_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,e,f
$C_5(i\text{-}Pr)_3$	$(1,2\text{-}CH_2CH_2)_2$	$(NMe_2)_2$	a,g
$C_5H(c\text{-}C_6H_{11})_3$	$1,2\text{-}CH_2CH_2$	NMe_2	a,b,e
$C_5H(2\text{-pentyl})_3$	$1,2\text{-}CH_2CH_2$	$N(n\text{-}Bu)_2$	a,c,e
C_5Et_4	$1,2\text{-}CH_2CH_2$	NMe_2	a,h
$C_5(n\text{-}Pr)_4$	$1,2\text{-}CH_2CH_2$	NMe_2	a
$C_5H_2(Cme_2Ph)_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a
$C_5H_2(C(Me)_2CH_2CH_3)_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,i
$C_5H_2(C(Me)(Et)CH_2CH_3)_2$	$1,2\text{-}CH_2CH_2$	NMe_2	a,i
C_5Me_4	$1,2\text{-}CH_2CH_2$	$NMe(CH_2)_2NMe_2$	a
C_5Me_4	$1,2\text{-}CH_2CH_2$	$NMe(CH_2C_3H_5O_2)$	a
C_5Me_4	$1,2\text{-}CH_2CH_2$	PPh_2	a
C_5Me_4	$1,2\text{-}CH_2CH_2$	PMe_2	a
C_5Me_4	$\text{-}SiMe_2CH_2\text{-}$	PPh_2	a
C_5Me_4	$\text{-}SiMe_2CH_2\text{-}$	PMe_2	a
C_5Me_4	$\text{-}CH_2SiMe_2\text{-}$	$N(n\text{-}Bu)_2$	a
$C_5H_2(CH_2CH(Ph)CH_3)_2$	$1,2\text{-}CH_2CH_2$	NMe_2	j
Ind	$1,2\text{-}CH_2CH_2$	NMe_2	k
2-MeInd	$1,2\text{-}CH_2CH_2$	NMe_2	k
3-MeInd	$1,2\text{-}CH_2CH_2$	NMe_2	k
Flu	$1,2\text{-}CH_2CH_2$	NMe_2	l

[a] J.A.M. van Beek, G.J.M. Gruter, Eur. Pat. Appl. 805,142 (1997).

[b] G.J.M. Gruter, J.A.M. van Beek, PCT Int. Appl. 97/42148 (1997).

[c] G.J.M. Gruter, J.A.M. van Beek, J.G. De Vries, PCT Int. Appl. 97/42151 (1997).

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[k] G.J.M. Gruter, J.A.M. van Beek, M. Herklots, PCT Int. Appl. 97/42164 (1997).

[l] G.J.M. Gruter, J.A.M. van Beek, M. Herklots, PCT Int. Appl. 97/42165 (1997).

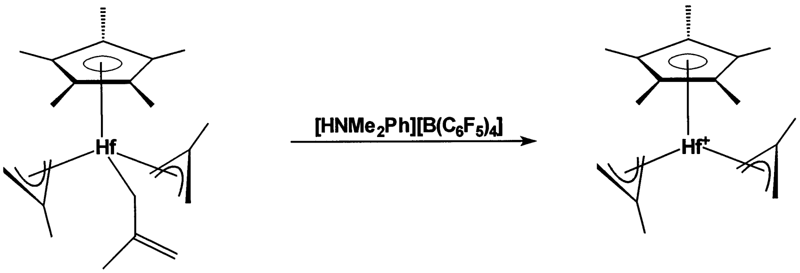


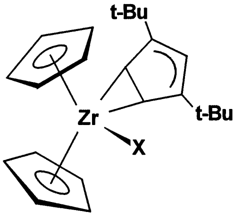
Fig. 18. Generation of cationic (cyclopentadienyl)bis(allyl)hafnium catalyst.

In the presence of MAO, the cyclopentadienyl titanium thiolate complexes $Cp^*TiCl_2(SC(SiMe_3)_3)$ [76] and $Cp_2Ti(SCH_2CH_2PMe_2)_2$ [77] afford polyethylene at a catalyst activity of about 150 g $mmol^{-1}$ Ti. The binuclear complex $Cp_2Zr(Cl)–O(CH_2)_6O–(Cl)ZrCp_2$ probably dissociates into mononuclear zirconocene active centers when allowed to react with MAO for ethylene-1-butene copolymerizations [78].

Metallocene complexes bearing bidentate reactive ligands include $CpZr(S_2COEt)_3$ [79] and $CpZr(S_2P(OEt)_2)_3$ [80], used with MAO in ethylene polymerization. The tris(diethylcarbamate) complex $(Ind)Zr(O_2CNEt_2)_3$ and the tris(benzoate) complex $(Ind)CH_2CH_2(Ind)Zr(O_2CPh)_3$ form catalysts with MAO to copolymerize ethylene with 1,7-octadiene, vinylnorbornene, or norbornadiene to copolymers with long-chain branching [81].

Among carbon-based reactive ligands, the allyl complex Cp*Zr(1,2,3-trimethylallyl)Br_2 cocatalyzed by MAO copolymerizes ethylene and 1-octene in a solution process [82]. Cp*Hf(2-methylallyl)Me_2, allowed to react with $B(C_6F_5)_3$, forms [Cp*Hf(2-methylallyl)Me][$MeB(C_6F_5)_3$], which is active for ethylene polymerization. In the presence of $[HNMe_2Ph][B(C_6F_5)_4]$, Cp*(2-methylallyl)$_3$ is ionized to the cationic bis(2-methylallyl) hafnium complex, which polymerizes ethylene and oligomerizes propylene to atactic products (Fig. 18) [83].

When 1,2-Et$(H_4–Ind)_2Zr(\eta^2-Me_3SiC{=}CSiMe_3)$ is allowed to react with two equivalents of ethylene, the zirconacyclopentane complex 1,2-Et$(H_4–Ind)_2Zr(CH_2)_4$ is formed. This is an effective catalyst for ethylene polymerization when activated by $B(C_6F_5)_3$ (Fig. 19) [84]. The complex $Cp_2ZrX(\eta^2-C_5H_3(t\text{-Bu})_2)$ (**20**; X = Cl, Br) is polymerization inert, but an active system for ethylene polymerization is produced when the compounds are allowed to react with MAO [85].



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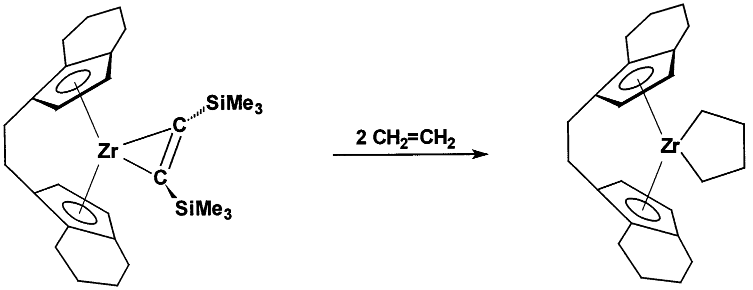


Fig. 19. Synthesis of metallacyclopentane zirconocene procatalyst.

7. Binuclear complexes

Metallocene catalyst systems containing more than one metal center have the potential to create polymers with controlled breadth of molecular weight distribution and comonomer distribution through differing metal centers, different ligand environments, or both. The consequences of interactions between two polymerization centers in close proximity is a fascinating area of potential study as well.

Reaction of two equivalents of zirconocene dichloride with butyllithium affords the dimeric Zr(III) complex $(CpZr)_2(\mu\text{-}Cl)_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$, which functions as a polymerization catalyst homogeneously (with MAO) or heterogeneously (supported on clays and activated with $Al(i\text{-}Bu)_3$) (Fig. 20) [86].

As an example of interactions of adjacent metal sites, reaction of the tetramethyl zirconium fulvalene complex $(Cp'ZrMe_2)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ with $B(C_6F_5)_3$ at low temperatures affords a cationic dizirconium trimethyl complex containing a bridging methyl group. At more elevated temperatures, methane is lost and a binuclear $\mu\text{-}CH_3$, $\mu\text{-}CH_2$ complex is formed (Fig. 21). This still functions as an ethylene polymerization catalyst, albeit one with very low activity [87].

Binuclear complexes in which the cyclopentadienyl rings are bridged by dimethylsiloxane groups of varying lengths are represented by complexes like $[TiCl_3CpSiMe_2]_2(\mu\text{-}SiMe_2O)$ [88] and $[(Ind)ZrCl_2CpSiMe_2]_2(\mu\text{-}(SiMe_2O)_n)$ [89] (n =

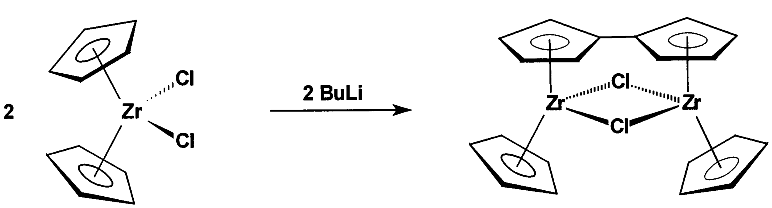


Fig. 20. Formation of binuclear Zr(III) complex.

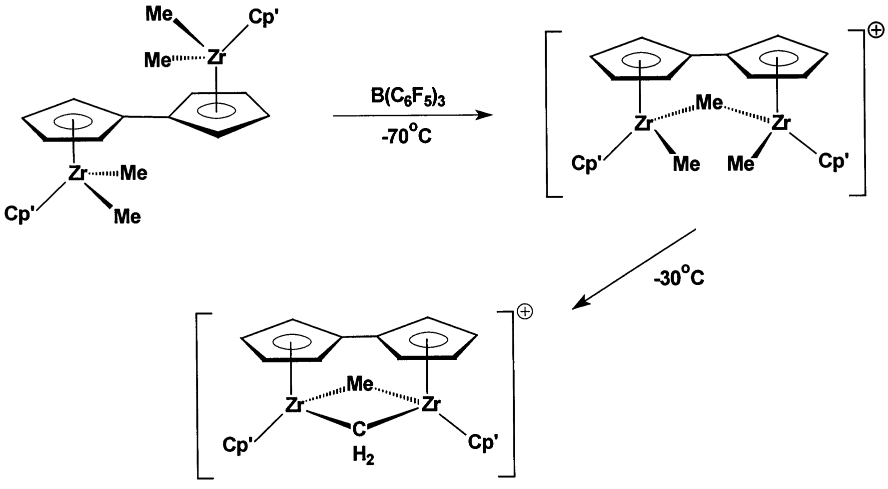
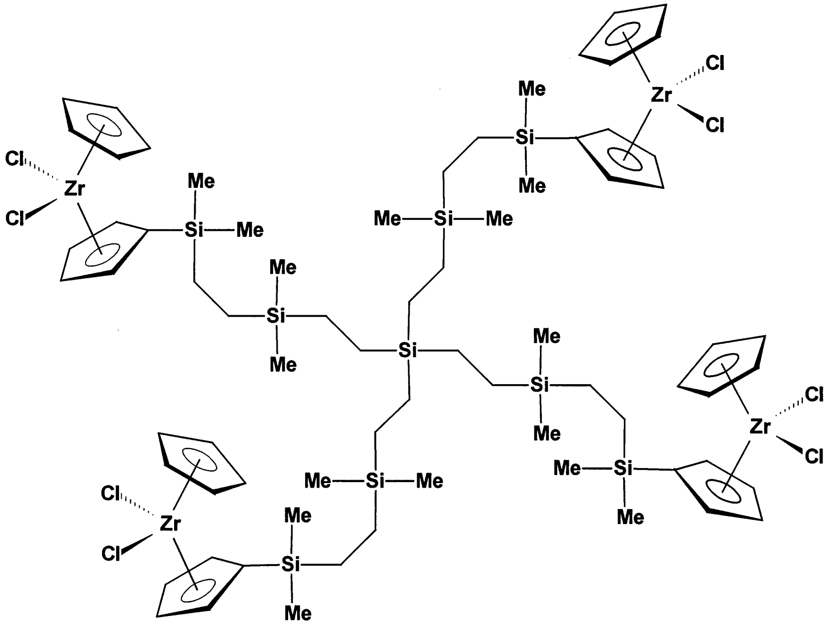


Fig. 21. Reactions of dinuclear zirconocene alkyls

1–3). The titanium complex polymerizes styrene to s-PS with a narrow molecular weight distribution and better syndiospecificity than $CpTiCl_3$; bimodal molecular weight distribution s-PS is obtained when the catalyst is used in conjunction with $CpTiCl_3$ or Cp^*TiCl_3. The binuclear zirconocene complexes exhibit lower activities than $(Ind)(Cp)ZrCl_2$, but afford polymers of higher molecular weight.

Dendrimeric multinuclear complexes like **21** are produced when multiarmed silane hydrides such as $Si(CH_2CH_2SiMe_2H)_4$ are allowed to react with metallocenes containing vinylic groups (e.g. $(CH_2 = CH)SiMe_2C_5H_4(Cp)ZrCl_2)$ in the presence of a platinum catalyst.



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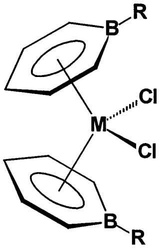
These complexes may be used for the polymerization and copolymerization of ethylene and α-olefins when cocatalyzed by MAO [90].

8. Ancillary ligands isolobal to cyclopentadienide

Among the ancillary ligands isolobal to cyclopentadienide, metal complexes of the boratabenzene anion were the most studied in 1997. The reactivity of catalysts like **22** is strongly dependent on the group bonded to the boron atom.

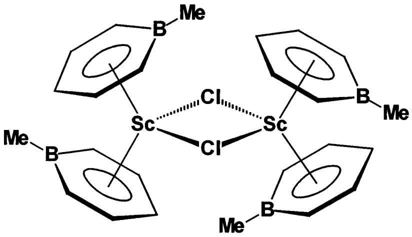


22

When R = N(i-Pr)$_2$, MAO-cocatalyzed reactions with ethylene produce high molecular weight polyethylene, catalysts with R = Ph afford oligomeric products containing both 1-olefin end groups and internal vinylidene groups [91]. The latter are produced by reincorporation of α-olefin into a metal alkyl chain, followed by immediate β-H chain termination. When R = OEt, only α-olefins are produced [92].

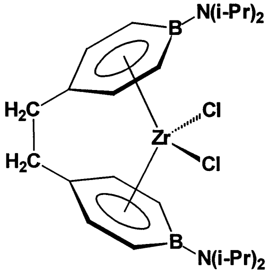
Mixed cyclopentadienyl-boratabenzene complexes such as Cp′(C_5H_5BMe)MCl_2, (Cp = Cp, Cp*, M = Ti, Zr, Hf) can be prepared from Cp′MCl_3 and 2-(Me_3E)C_5H_5BMe (E = Si, Sn) [93]. The mono(boratabenzene) complex (C_5H_5BMe)$TiCl_3$ is stable, but the zirconium analogue slowly disproportionates to $ZrCl_4$ and $(C_5H_5BMe)_2ZrCl_2$. When combined with MAO, these complexes are effective catalysts for ethylene polymerization [94].

The dimeric scandium and gadolinium bis(boratabenzene) complexes (**23**) were synthesized from MCl_3 and Li[C_5H_5BMe]; ethylene is polymerized when butyloctylmagnesium is used as a cocatalyst [95]. (C_5H_5BMe)$TaCl_4$, prepared from 2-(Me_3Sn)(C_5H_5BMe) and $TaCl_5$ was also reported in this disclosure.



23

Propylene polymerization using bridged bis(boratabenzene) complexes like **24** yield largely atactic polymer [96]; apparently these complexes either lack chirality or have insufficient chirality to induce stereospecific propylene insertion.



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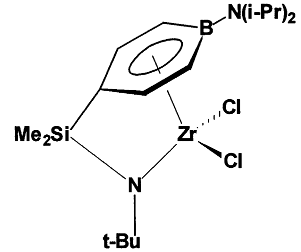
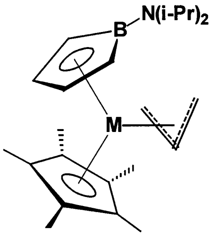
The bridged amido complex **25** was used to copolymerize ethylene and 1-octene, but comonomer incorporation was rather low (0.8–1.0 mol%).



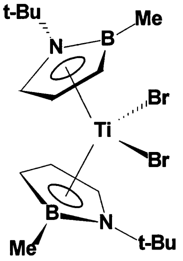
25

The borole ligand is a dianionic 6π surrogate for the Cp ligand. The neutral allyl complexes of zirconium and hafnium (**26**) function as single-component polymerization catalysts, but the small-scale experiment used precludes comparison to the bis(cyclopentadienyl) analogues [97].



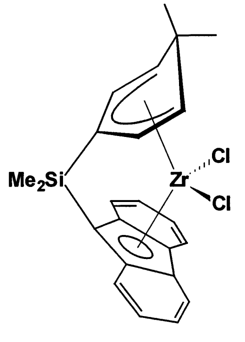
26

The bis(azaborolinyl)titanium complex **27** polymerizes ethylene with an MAO cocatalyst, but the activity is relatively low (1.56 kg mmol^{-1} Ti·h^{-1}·atm.) [98].



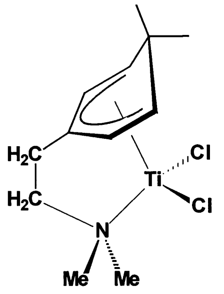
27

Pentadienyl ligands, both open and closed, were used as ancillary ligands for single-site olefin polymerization procatalysts. Bridged pentadienyl-cyclopentadienyl zirconium complexes like **28** were combined with MAO to polymerize ethylene [99].



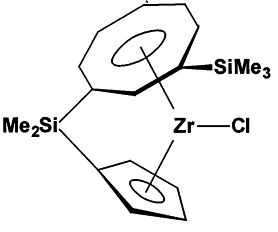
28

The dimethylcyclohexadienyl titanium complex **29** resembles the cyclopentadienyl complex (Section 5), but no polymerization experiments were reported in the disclosure [100].



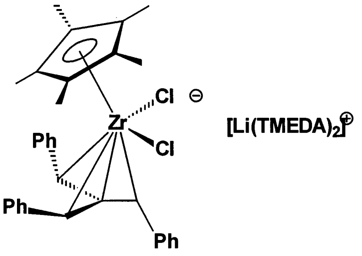
29

The cyclooctatetraenyl dianion was employed as a polymerization-stable ancillary ligand in (COT)ZrCl$_2$ (or its dimer), which, when combined with MAO, forms an ethylene polymerization catalyst [101]. Polymer yields were negligible when either AlMe$_3$ nor AlEt$_3$ were used as cocatalysts. The complex (COT)$_2$Zr was also used with MAO to polymerize propylene to isotactic polymer (m.p. 135°C), though no details were provided of the active polymerizing species in this catalyst [102]. The bridged cyclooctatetraenyl-cyclopentadienyl zirconium complex **30** polymerizes ethylene or propylene to polymers with narrow molecular weight distributions (MW/Mn = 2.4–2.7) [103].



30

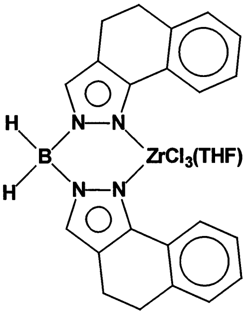
Bazan has used the dianionic trimethylenemethane ligand in preparing $[Li(TMEDA)_2][Cp'Zr(TMM)Cl_2]$ (Cp′ = Cp, Cp*) and Cp*Zr(TMM)Me(THF) complexes, which, when activated by MAO, polymerize ethylene, 1,5-hexadiene, and propylene [104]. The most active catalyst is $[Cp^*Zr(C(CH_2Ph)_3Cl_2]^-$ (**31**), whose superior performance is attributed to the steric bulk of the ligands delaying the deactivation of the $Cp^*Zr(C(CH_2Ph)_3)Me$ active catalyst species to an inactive $Cp^*Zr(C(CH_2Ph)_3)(\mu\text{-}CH_2)$ byproduct.



31

$(C(NPh)_3)TiCl_2$ has also been reported to polymerize ethylene in the presence of MAO [105].

(Pyrazolyl)borate metal complexes continue to be of interest as polymerization catalysts. It has been suggested that bis- and tris(pyrazolyl)borate complexes with bulky substitutents in the 3-position—such as **32**—are more active than those complexes with smaller or no substituents [106].



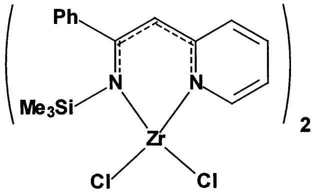
32

9. Non-cyclopentadienyl anionic ancillary ligands

A second class of polymerization-stable ancillary ligands for single-site catalysts comprises ligands which cannot be considered π-bonded ligands like cyclopentadienides and their isolobal equivalents. These can be broadly divided into complexes with chelating monoanionic ligands having the general formula L_2MCl_2 and chelating dianonic ligands with the general formula $(L)MCl_2$.

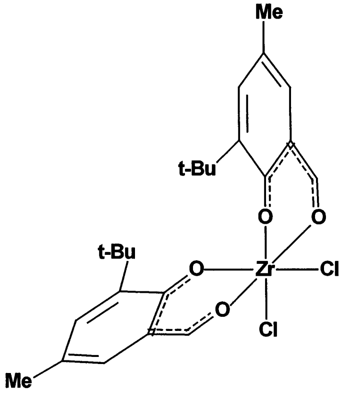
Acetylacetonate complexes of the Group 4 metals are an example of the former class which quickly come to mind, and investigators at Borealis have allowed *cis*-(1,3-diphenyl-1,3-propanedionato)titanium dichloride to react with MAO to give a catalyst for ethylene polymerization [107]. β-Diketonate titanium dichlorides supported on $MgCl_2$ can be activated by MAO or trialkylaluminums to generate catalysts for polymerizing propylene to mixtures of isotactic (heptane insoluble) and atactic (heptane soluble) polymers [108]. The zirconium analogues are almost inactive. Supporting the catalyst increases activities 400-fold over the homogeneous version.

Related to the β-diketonates are metal complexes with β-diketemine ligands like **33**.



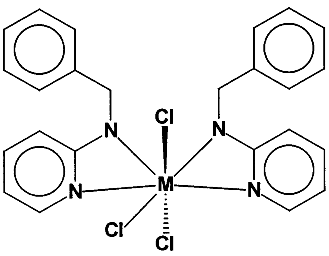
33

The ligand was prepared by deprotonation of 2-trimethylsilylmethylpyridine by butyllithium followed by reaction with benzonitrile. The zirconium complex polymerizes ethylene in the presence of MAO [109]. Likewise, bis(salicaldehyde)MCl_2 complexes such as **34** exhibit moderate (8 kg g^{-1} M·h^{-1}, M = Zr) to good (80 kg g^{-1} M·h^{-1}, M = Ti) activities in ethylene polymerization [110].



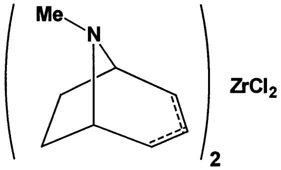
34

2-Hydroxypyridine complexes of titanium $(2\text{-}OPy)_2TiCl_2$, prepared from the alkoxide and $TiCl_4$, polymerize ethylene and copolymerize ethylene and 1-hexene in the presence of MAO [111]. The related 2-benzylamidopyridine complexes of tantalum and niobium (**35**) were synthesized by the reaction of the amine with MCl_5; the tantalum derivative polymerizes ethylene with high activity to polyethylene of narrow MWD [112].



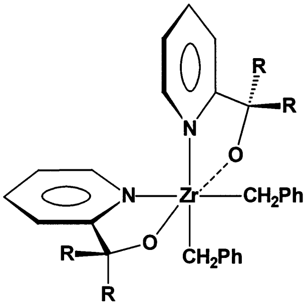
35

The bis(tropidinyl)zirconium complex **36** is prepared from the reaction of the trimethylstannyl derivative of tropidine with $ZrCl_4(THF)_2$ in CH_2Cl_2; with MAO, it polymerizes ethylene with an activity about 14 times less than Cp_2ZrCl_2–MAO [113].



36

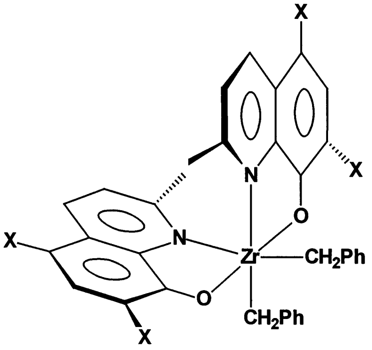
The 2-alkoxypyridine complexes $(pyCR^1R^2O)Zr(CH_2Ph)_2$ ($R^1R^2 = (CF_3)_2$, $H(CF_3)$, Me_2) and $(pyCAr_2O)M(NMe_2)$ (**37**; M = Ti, Zr, Hf) were synthesized from the alcohol and $Zr(CH_2Ph)_4$ [114] and $M(NMe_2)_4$ [115], respectively.



37

Both complexes have *cis*-N, *trans*-O, *cis*-R structures. The stereoisomers interconvert readily in solution. The cations derived from the reaction of $(pyCR^1R^2O)Zr(CH_2Ph)_2$ with $B(C_6F_5)_3$ polymerize ethylene when $R^1R^2 = (CF_3)_2$, but the Me_2 derivative is inactive. The bis(amide) complexes also react with $Al(i\text{-}Bu)_3$ and MAO to give catalysts which polymerize ethylene to polyethylene with broad polydispersity; removal of the ligands by the cocatalyst may generate multiple active species.

The 8-quinolinato complexes like **38** are prepared from the reaction of 8-hydroxyquinolines with MR_4 (M = Zr, Hf; R = NMe_2, CH_2Ph, CH_2CMe_3, CH_2SiMe_3) or from the lithium alkoxides with $ZrCl_4$ [116].

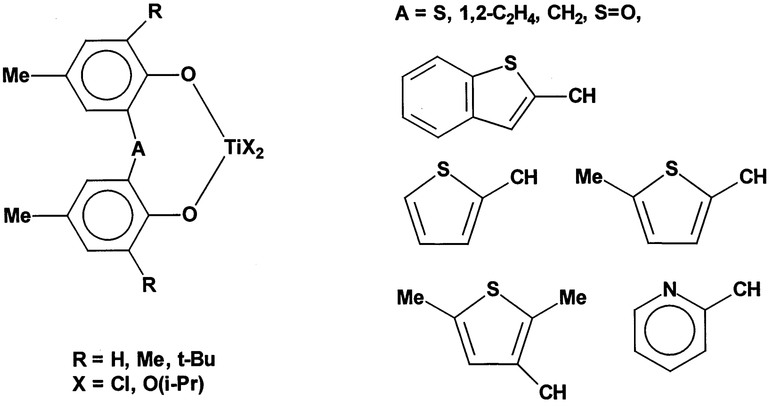


X = H, Br

38

As with the pyridine alkoxides, these have a *cis*-N, *trans*-O, *cis*-R solid-state structure, the stereoisomers of which racemize in solution. When activated by MAO, $B(C_6F_5)_3$, or $[HNMe_2Ph][B(C_6F_5)_4]$, the 5,7-dibromo-2-methyl-8-quinolinol-based complexes are polymerization active, while the 8-hydroxyquinaldine-based cations are catalytically inactive.

Chelating dianionic polymerization-stable anionic ancillary ligands for single-site catalysts are may be dialkoxides and diaryloxides, diamides, or these dianions with additional donor atoms. One popular diaryloxide ligand is the bridged diphenolate group. Mülhaupt, Okuda and co-workers have investigated ethylene-styrene copolymerizations using titanium bis(phenolate) complexes (**39**) with methylene, ethylene, sulfide, and sulfoxide groups bridging the phenolates [117].



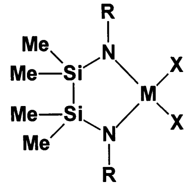
39

While catalyst activity declined in the order $S > SO > C_2H_4 \approx CH_2$, the 1,2-ethylene-bridged complex incorporated styrene comonomer the most efficiently of the catalysts. Research at Sumitomo explored the behavior of bis(phenolate)titanium complexes in which the bridging group was a sulfur- or nitrogen-containing methylene group [118]. These catalysts have activities far greater than that of analogous sulfur-bridged bis(phenolate)titanium catalysts.

The dimethylated (dianionic) derivative of [*p*-*t*-Bu-calix[4]arene] was deprotonated and allowed to react with $ZrCl_4(THF)_2$ to form [*p*-*t*-Bu-calix[4]$(OMe)_2(O)_2ZrCl_2$] which can be methylated to the zirconum dimethyl derivative. This reacts with $B(C_6F_5)_3$ to yield the cationic complex [*p*-*t*-Bu-calix[4]$(OMe)_2(O)_2ZrMe]^+[MeB(C_6F_5)_3]^-$ [119]. The reaction product of [*p*-*t*-Bu-calix[4]arene] with Ti(O-*i*-Pr)$_4$ polymerizes styrene to s-PS in the presence of MAO [120].

Chelating diamide ligand complexes include McConville's $[Ar(CH_2)_3Ar]ZrX_2$ compounds (Ar = 2,6-*i*-$Pr_2C_6H_3$, X = Cl, NMe_2, Me, CH_2Ph) which polymerize 1-hexene to high polymers when MAO is used as a cocatalyst, but form only oligomers when activated by $[Ph_3C][B(C_6F_5)_4]$ [121]; the catalyst activity is some 2000 times slower than that of the analoguous titanium complex. The titanium cation [1,3-(2,6-(*i*-Pr)$_2C_6H_3)_2(CH_2)_3TiMe]^+[MeB(C_6F_5)_3]^-$, an excellent catalyst for living 1-hexene polymerization, decomposes in the absence of monomer to the inactive byproduct 1,3-(2,6-*i*-$Pr_2C_6H_3)_2(CH_2)_3Ti(C_6F_5)(CH_2B(C_6F_5)_2)$ [122].

The metallacyclodisiladiazane complexes of titanium and zirconium (**40**) polymerize ethylene in the presence of 800 equivalents of MAO.

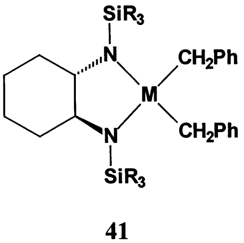


R = t-Bu, 2,6-(i-Pr)$_2C_6H_3$, 4-FC_6H_4
M = Ti, Zr
X = Cl, F

40

The titanium complexes are more active than when zirconium is the metal center and among the titanium complexes activity decreases as X varies from Me > Cl > F. The last of these is a dimer; variations in activity may be explained by difficulties in generating the active catalytic species [123].

$Ti(CH_2Ph)_4$ reacts with *N*-silyl-substituted *trans*-1,2-diaminocyclohexane to produce the dibenzyl complex **41** [124] while the reaction of the amide dianion with $ZrCl_4(THF)_2$ affords the bis(diamide) compound $(1,2-(Me_3SiN)_2C_6H_{10})_2Zr$ (**42**) [125].



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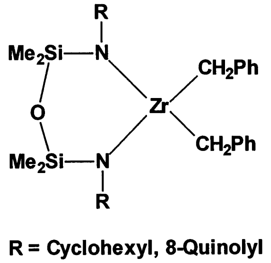
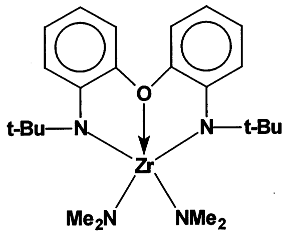


42

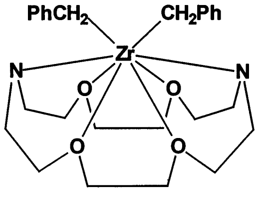
The zirconium complex polymerizes ethylene in the presence of MAO, as does the dibenzyl compound formed from the reaction of $Zr(CH_2Ph)_4$ with *N*-substituted aminodimethylsilylethers.

The tridentate diamine ligand (*t*-BuNH-*o*-Ph)$_2$O reacts with $Zr(NMe_2)_4$ to afford [(*t*-BuN-*o*-Ph)$_2$O]Zr(NMe$_2$)$_2$ (**43**) [126].



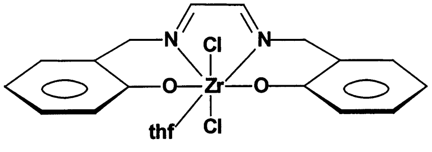
43

A cationic complex [(*t*-BuN-*o*-Ph)$_2$O)ZrMe]$^+$[MeB(C_6F_5)$_3$], formed from the dimethyl derivative and $B(C_6F_5)_3$ polymerizes ethylene in toluene or chlorobenzene. 1-Hexene is polymerized to poly(1-hexene) of very narrow MWD (1.02–1.14), suggesting ‘living’ polymerization. Compound **44**, prepared from 4,13-diaza-18-crown-6 and $Zr(CH_2Ph)_4$, forms a mono(benzyl) cation on reaction with $B(C_6F_5)_3$; this catalytically dimerizes *p*-tolylacetylene to (*Z*)-1,4-di-*p*-tolyl-1-buten-3-yne [127].



44

Dialkoxide ligands containing nitrogen donors are represented by the ethylenediamine(salicylideneiminato)zirconium complex **45** [128] and the pyridine alkoxide complex **46** [129].



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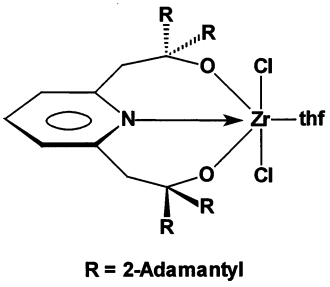
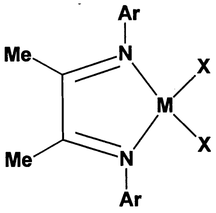


46

The former complex was supported on silica and activated with MAO to form a catalyst which polymerizes ethylene with moderately high activity (200–500 g PE $mmol^{-1}$ $Zr \cdot h^{-1}$). When contacted with $Al(i\text{-}Bu)_3$–$[Ph_3C][B(C_6F_5)_4]$, the latter complex polymerizes ethylene to very high MW polymer (MW = 1 320 000, MWD = 2.7).

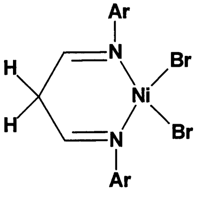
10. Neutral ancillary ligands

Cationic complexes derived from α-diimine ligands and nickel or palladium centers have attracted considerable interest because of the highly branched ethylene homopolymer they produce. The procatalysts have been dihalide or dialkyl complexes as in **47**.



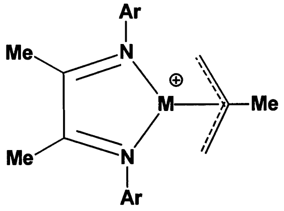
47

Catalysts with bulky Ar groups such as $2,6\text{-}(i\text{-}Pr)_2C_6H_3$ form polymers, but aryl groups of more modest steric demand such as $-C_6H_5$ or $-C_6H_4$-4-Me do not retard chain transfer and give linear α-olefin products [130]. Weakly ligated palladium dications such as $[Pd(CH_3CN)_4][BF_4]_2$ and $Pd(OAc)_2$-HBF_4 in the presence of the diimide also form active catalysts [131]. The nickel complex of the β-diimine ligand (**48**, Ar = $2,6\text{-}(i\text{-}Pr)_2C_6H_3$) was also prepared and tested as catalysts, producing a more linear polymer at lower catalyst activity, attributed to the larger ring chelate.



48

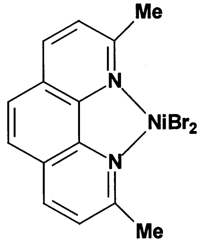
In combination with $AlEt_2Cl$, the PF_6^- salts of the cationic nickel methylallyl complexes of 1,2-bis(2,6-diisopropylphenylimido)ethane (**49**) polymerize ethylene in a chlorobenzene medium to low-crystallinity homopolymer [132].



49

The catalysts function most effectively at lower temperatures: above about 25°C, the catalysts lose activity. Polymer crystallinity decreases with increasing temperature.

Other chelating ligands have successfully been used with nickel halides in forming ethylene polymerization catalysts, including 2,9-dimethylphenanthroline (**50**) [133], [2.2](2,6)-pyridinophane (**51**) [134], and 1,1′-bis(diphenylphosphino)ferrocene (**52**) [135].



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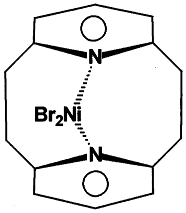

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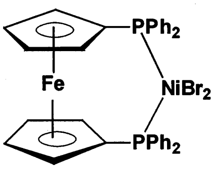

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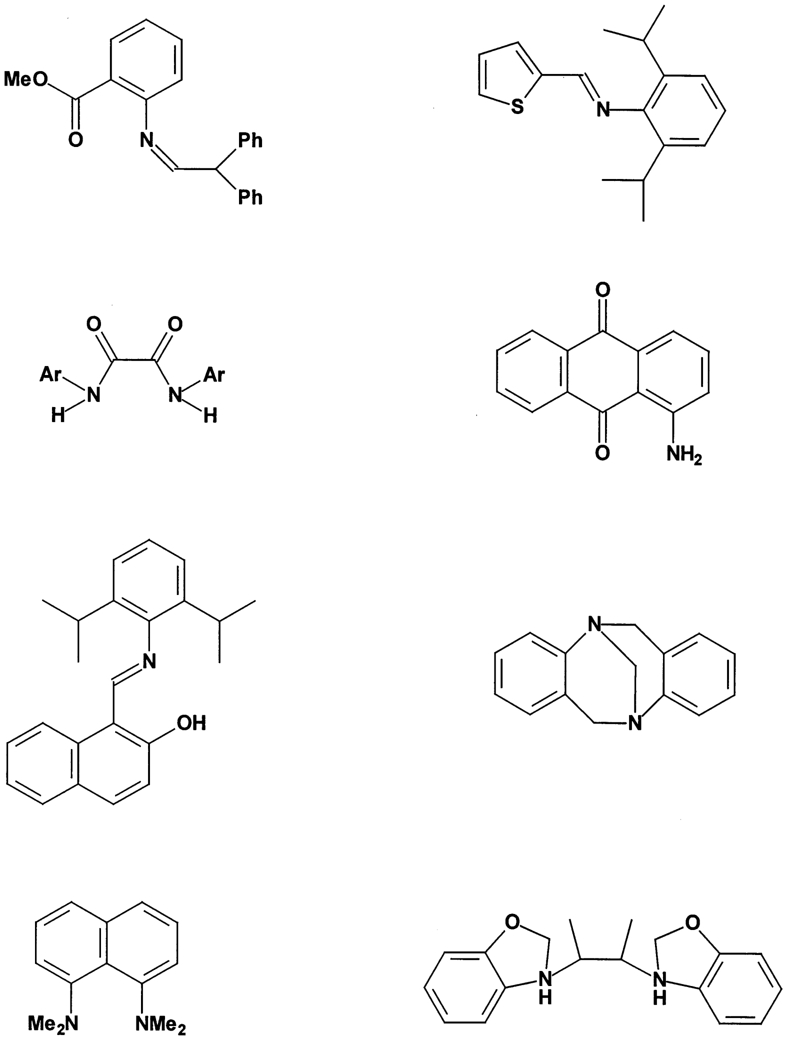
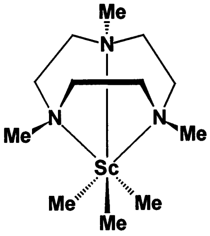


Fig. 22. Neutral ligands used in Ni(II) catalysts for olefin polymerization [136].

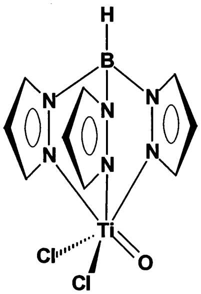
Catalysts have also been generated from allyl nickel chloride dimer and Na[B(3,5-$(CF_3)_2C_6H_3)_4$] in the presence of an extensive range of mono- and bidentate ligands, a representative sampling of which are illustrated (Fig. 22) [136].

The 1,4,7-trimethyl-1,4,7-triazacyclononane ligand was allowed to react with $ScCl_3(THF)_3$ to yield (tmtacn)$ScCl_3$, which was subsequently allowed to react with MeLi to form the trimethyl complex (tmtacn)$ScMe_3$ (**53**).



53

An active polymerization catalyst is formed in the presence of $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$ [137]. Tris(pyrazolyl)methane reacts with $TiCl_4(THF)_2$ to form $HC(C_3H_3N_2)_3Ti(=O)Cl_2$ (**54**).



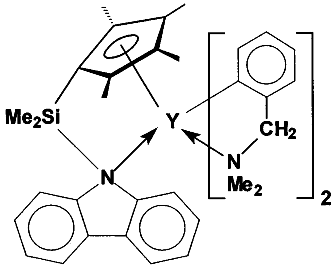
54

This complex can be combined with MAO to afford a catalyst which is active for the polymerization of ethylene, though no polydispersity data were available [138].

11. Single-site catalysts of the Group 3 metals and lanthanides

The sterically very crowded complex $(\eta^5\text{-Cp}^*)_3Sm$ polymerizes ethylene to polyethylene of extremely high molecular weight. The authors speculate that one of the rings either slips to form an η^1-Cp* complex which inserts ethylene (Fig. 23) or eliminates tetramethylfulvene to form a catalytically-active Cp^*_2SmH species [139].

The dimethylsilyl-bridged cyclopentadienyl carbazole yttrium complex **55** was prepared from the neutral ligand $Me_2Si(C_5Me_4H)(NC_{12}H_8)$ and $Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3$.



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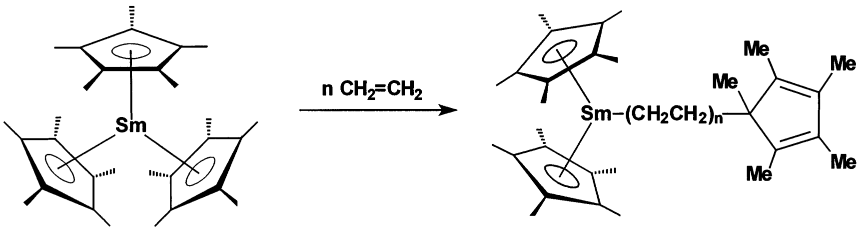


Fig. 23. Proposed mechanism for catalyst initiation by Cp_3^*Sm

This serves as a one-component system for preparing vinyl-terminated polyolefin macromers, which can subsequently be copolymerized with ethylene using a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$–$B(C_6F_5)_3$ catalyst [140].

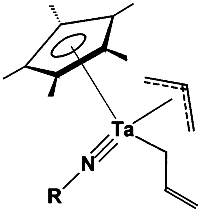
A solid polymerization catalyst has been prepared by allowing $Cp_2^*NdCH(SiMe_3)_2$ to react with BuMgEt and $MgCl_2$. This was used to polymerize ethylene to high-MW HDPE [141].

The cationic complex $[(t\text{-}BuCp)_2Yb(THF)_2][BPh_4]\cdot THF$ was reported to polymerize styrene to high molecular weight polystyrene, but the polymer is completely soluble in methyl ethyl ketone, indicating a lack of stereospecificity [142]. The bimetallic alane complex $Cp'_2YbAlH_3\cdot L$ ($Cp' = t$-BuCp, Cp*; $L = NEt_3$, THF, Et_2O) also polymerizes styrene, but not α-olefins like ethylene and propylene. Indeed, addition of these monomers suppress styrene polymerization activity completely by hydroaluminating and converting the metal component to an inactive Cp'_2YbAlR_3 complex [143].

12. Single-site catalysts of the Group 5 and 6 metals

1,3-Butadiene is polymerized to mostly *cis*-1,4 polybutadiene by the trivalent vanadium complex $(MeCp)VCl_2(PEt_3)_2$ in combination with $Al(i\text{-}Bu)_3$–$[HNMe_2Ph][B(C_6F_5)_4]$ [144], or by the V(IV) compound $CpVCl_3$ combined with MAO [145] while the formally V(V) complex $(PhN{=})VCl_3$ with MAO affords polybutadiene with comparable contents of *cis*- and *trans*-1,4 and 1,2- placements [146].

When R = 2,6-diisopropylphenyl, the tantalum η^1,η^3-diallyl imido complex **56** polymerizes ethylene when allowed to react with $[Ph_3C][B(C_6F_5)_4]$ (but not $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$) while the dichloride analogue is inactive in the presence of excess MAO.



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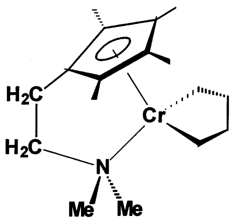
In contrast, when R = Si(*t*-butyl)$_3$, the dichloride complex is polymerization active while the diallyl complex is inactive when allowed to react with the boron activators [147].

The chemistry of homogeneous cyclopentadienyl chromium catalysts for olefin polymerization was reviewed by Theopold [148]. The chromacyclopentane complex **57** functions as an active polymerization catalyst (16 kg mmol^{-1} Cr·h^{-1}) in the presence of a surprisingly low excess of MAO (Al:M = 100).



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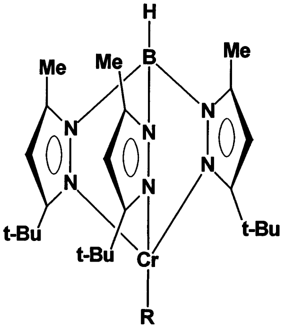
The intermediacy of an η^2-CH$_2$=CH$_2$ complex was suggested by Cp*Cr(PMe$_3$)$_2$(η^2-CH$_2$=CH$_2$), which polymerizes ethylene at room temperature and 50 bar [149]. In contrast, the tris(pyrazolyl)borate Cr(II) alkyls **58** (R = Et, Ph, CH$_2$SiMe$_3$) are unreactive toward ethylene and attempts to oxidize the complexes to Cr(III) species using [Cp$_2$Fe][BPh$_4$] results only in the loss of the alkyl group [150].



58

Rather surprisingly, Cp$_2$NbCl$_2$ and even Cp$_2$WCl$_2$ exhibit some activity in ethylene polymerization when cocatalyzed by MAO [151]. The activities (100 g mmol^{-1} M·h^{-1}) are vastly lower than that of Cp$_2$ZrCl$_2$ (6000 g mmol^{-1} Zr·h^{-1}). Active site counting using tritiated methanol indicates that while some 87% of zirconocene centers are activated by MAO, only 0.5% of Cp$_2$WCl$_2$ is similarly activated.

13. Polymerization catalysts of the late transition metals

Section 10 detailed much of the progress in new catalysts of the late transition metals, but some other disclosures should be noted. A study of cocatalyst effects on the polymerization behavior of (ArN=CR–CR=NAr)NiX_2 catalysts (R = H, Me; Ar = 2,6-(i-Pr)$_2C_6H_3$, 2,6-$Me_2C_6H_3$) indicated that MAO afforded catalysts of greater activity than did $AlEt_2Cl$ [152]. The degree of branching was also dependent on cocatalyst (Table 2): ion-pair catalysts with more coordinating anions (BF_4^-, $AlMe_4^-$) give a greater degree of branching than less coordinating anions like $B(C_6F_5)_4^-$.

Polymerization of ethylene at high temperatures (120–180°C) and pressures (1300–1800 bar) using a (ArN=C(R)–C(R′)=NAr)NiBr_2–MAO catalyst (Ar = 2,6-(i-Pr)$_2C_6H_3$; R = R′ = Me, R-R′ = acenaphthyl) produces polymers with extensive chain branching, far more than that predicted from the low temperature and pressure performance of these catalysts [153].

An inverse isotope effect was detected in the cobalt catalyst [Cp*(P(OMe)$_3$)CoCH_2CH_2-μ-H][B(3,5-(CF_3)$_2C_6H_3$)$_4$], with catalyst activity greater when C_2D_4 was the monomer rather than C_2H_4 ($k_H/k_D = 0.48$), associated with the release of the β-agostic bond (Co···H···C vs. Co···D···C) in the catalyst resting state [154]. The effect does not arise from the relative reactivity of the catalyst with C_2H_4 versus C_2D_4: polymerization of a mixture of the two monomers affords a polymer matching the feed ratio.

14. Catalysts without transition metals

Ziegler's discovery of metal-mediated olefin polymerization came out of research on 'Aufbau' reactions of ethylene with aluminum alkyls. Almost 50 years later, Jordan showed that aluminum amidinate complexes react with $B(C_6F_5)_3$ or [Ph_3C][$B(C_6F_5)_4$] to form cationic species which polymerize ethylene to HDPE with narrow molecular weight distribution (Fig. 24); the intermediate discovery of degradation-resistant non-interfering anions assist in forming a stable polymerizing catalyst [155].

Table 2
Ethylene polymerization by (ArN=CH–CH–NAr)NiMe_2 catalyst (Ar = 2,6-(i-Pr)$_2C_6H_3$)

Cocatalyst	Branches per 1000 carbons	Melting point (°C)
$B(C_6F_5)_3$	18	128
[Ph_3C][$B(C_6F_5)_4$]	6	137
$HBF_4 \cdot OMe_2$	15	137
$AlMe_3$	82	122
MAO	25	123

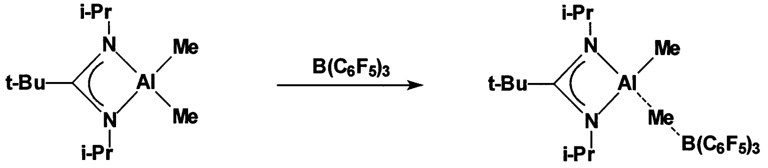


Fig. 24. Cationic aluminum amidinate catalyst for olefin polymerization.

Remarkably, Cp^*_2Ca was reported to polymerize ethylene in the presence of $Al(i\text{-}Bu)_3$ and BuLi (possibly forming $[AlBu_4]^-$). The mechanism by which chain growth takes place is not clear, and catalyst activities are quite low (16 g mol catalyst·h^{-1}·atm.) [156].

15. Activator compounds

Most single-site catalysts are comprised of two ingredients, the metal component, upon which most of the attention falls, and the activating cocatalyst. Included is research carried out on new activating species and improved preparations of known cocatalysts, especially those directed toward commercial production.

MAO, the product of the controlled hydrolysis of trimethylaluminum and water, remains the most frequently used cocatalyst in single-site catalysis. It has been shown to be a superior cocatalyst to other hydrolyzed aluminum alkyls. For example, the activities of ethylene–norbornene copolymerizations by $Me_2SiCp_2ZrCl_2$ are 10 times lower when mixed ethyl- and isobutylalumoxanes were used as the cocatalyst rather than MAO, though more norbornene was incorporated into the copolymer [157]. Attempts to find substitutes continue, though: an investigation at Montell has found that hydrolyzed mixtures of branched trialkylaluminums like tris(2,4,4-trimethylpentyl)aluminum and tri(isobutyl)aluminum afford more active catalysts with $Et(H_4\text{–}Ind)_2ZrCl_2$ than alumoxanes based on either aluminum alkyl alone [158].

Methylalumoxane is a commercially available material. A number of continuous processes for its synthesis from $AlMe_3$ and water in an aromatic hydrocarbon have been described which ensure steady-state concentrations of MAO and residual $AlMe_3$ [159]. A low temperature (−10°C) hydrolysis followed by treatment of residual solids with $AlMe_3$ at higher temperatures (20−50°C) are reported to afford high yields of MAO [160]. The sonication of $AlMe_3$ with an aqueous LiCl solution speeds the hydrolysis process and yields an MAO solution which is more stable to gel formation [161]. The activity of a $Cp^*Ti(OMe)_3$–MAO catalyst is maximized by adjusting the ratios of MAO to free $AlMe_3$, as measured by ^{27}Al-NMR spectroscopy [162]. Pretreatment of $AlMe_3$ by CO_2 before hydrolysis yields a modified MAO composition with improved cocatalytic properties with respect to MAO from untreated $AlMe_3$ [163].

Further modifications of MAO are claimed to improve the performance of the cocatalyst. An increase in catalyst activity was observed when BHT [164] or siloxanes [165] are added to the MAO. The addition of methoxyboroxine to MAO affords a granular alumoxane product well suited to use in slurry polymerizations [166].

Alumoxanes and alumoxane surrogates can be generated from oxygen-containing compounds other than water. CO_2, benzophenone, and benzoic acid react with $AlMe_3$ to produce precursors which are converted to alumoxanes on heating [167]. Other protolytic agents used with trialkylaluminums to generate cocatalysts for polymerization by metallocene complexes include triphenylmethanol [168], tetrafluoroterephthalic acid [169], *t*-butyl-substituted phenols [170], bisphenols [171], and *t*-butylcatechol [172].

Despite their reputation as indefinite, non-stoichiometric materials, attempts to characterize alumoxanes continue. A study of MAO by multinuclear NMR spectroscopy found that the intensity of the MAO signal in the ^{27}Al-NMR spectrum increased on raising the temperature from ambient to 120°C. From the linewidths at these two temperatures, the nuclearity of $(MeAlO)_n$ species was estimated to be between 20 and 30 under ambient conditions and 9 to 14 at the higher temperature [173].

Tritto and co-workers have investigated the effect of added $AlMe_3$ on the molecular weight and polymerization performance of MAO [174]. MAO ‘free’ of $AlMe_3$ (containing about 1–7 mol% by titration with PPh_3) has a molecular weight of 1500–2700, while addition of 30 wt% $AlMe_3$ reduces the molecular weight to 480. Alumoxanes with lower molecular weights tended to have greater catalyst activities at $Al/Zr = 1000$; adding additional $AlMe_3$ tends to depress the molecular weight of the polyethylene formed.

Mesitylaluminum dihydride reacts with hexamethyltrisiloxane to form the cyclic tetramer $(Mes–AlO)_4$, characterized by X-ray crystallography. This reacts with AlR_3 (R = Me, Et) affording the ladder compound, also structurally characterized (Fig. 25). Unfortunately, neither alumoxane complex functions as a cocatalyst for ethylene polymerization with Cp_2ZrMe_2; it is felt that the size of the mesityl group inhibits interaction with the metallocene [175].

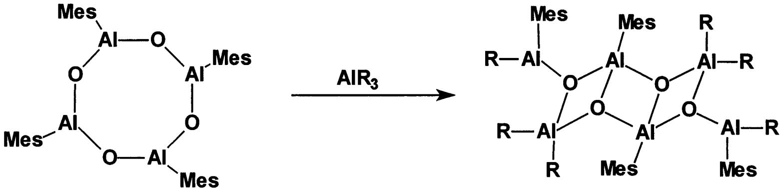
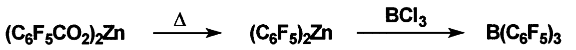


Fig. 25. Ladder alumoxane from $[Al(mes)O]_3$ and AlR_3.



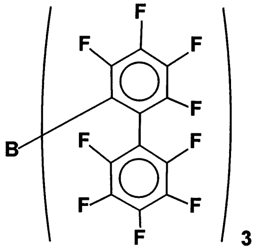
$$(C_6F_5CO_2)_2Zn \xrightarrow{\Delta} (C_6F_5)_2Zn \xrightarrow{BCl_3} B(C_6F_5)_3$$

Fig. 26. Synthesis of $B(C_6F_5)_3$ from zinc compounds.

Boron-based anions are the other major family of activators for single-site polymerization catalysts [176]. These may be derived from salts like $[Ph_3C][B(C_6F_5)_4]$ or from abstraction of an anion from the metal by $B(C_6F_5)_3$.

Both tetrakis(pentafluorophenyl)borate salts and tris(pentafluorophenyl)borane are commercially available reagents and research into new and more economical routes to these complexes is ongoing. The need to cool the reaction of an ethereal solution of C_6F_5MgX with BCl_3 is avoided when at least part of the reaction solvent has a higher boiling point [177]. $B(C_6F_5)_3$ has been prepared by extrusion of CO_2 from zinc pentafluorophenylbenzoate, followed by reaction of the organozinc product with BCl_3 (Fig. 26) [178].

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 (**59**) affords catalysts with greater activity than with $B(C_6F_5)_3$ [179].



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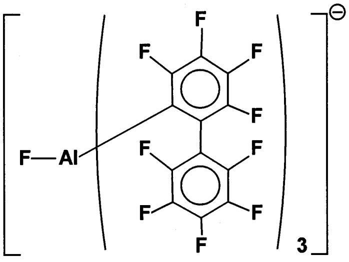
This has been ascribed to the lower coordinating strength of the $[MeB(C_{12}F_9)_3]^-$ anion with respect to the $[MeB(C_6F_5)_3]^-$ anion.

Tetrakis(pentafluorophenyl)borate salts can be made significantly (>5 wt%) soluble in aliphatic hydrocarbons by using tertiary ammonium salts with long-chain alkyl groups, for example $HN(C_{18}H_{37})_2(Me)^+$ [180]. Salts of metallocene cations with the 4-silyl-substituted $[B(4\text{-}C_6F_4SiMe_2\text{-}t\text{-}Bu)_4]^-$ and $[B(4\text{-}C_6F_4Si(i\text{-}Pr)_3)_4]^-$ anions exhibit greater solubilities and thermal stabilities than with $[B(C_6F_5)_4]^-$; activities of Cp'_2ZrMe^+ catalysts are higher with the silyl-substituted anions while $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)ZrMe^+$ catalysts are most active with $[B(C_6F_5)_4]^-$ [181]. Because of strong ion pairing, relatively uncrowded metallocenes like Cp_2ZrMe_2 and $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)MMe_2$ ($M = Ti$, Zr) are inert in ethylene polymerization at room temperature when activated by $[Ph_3C][FAl(C_{12}H_9)_3]$ (**60**), but become active at elevated temperatures; substituted Cp'_2ZrMe^+ catalysts are active under all conditions [182].



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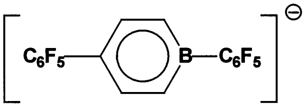
Substituted boratabenzene anions like **61** have also been suggested as suitable non-interfering anions for single-site catalysts, though no data on polymerization performance were reported [183].



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Reacting 1,4-dilithiotetrafluorobenzene with two equivalents of $ClB(C_6F_5)_2$ affords the binuclear Lewis acid activator **62** (Fig. 27).

Further reaction with one equivalent of $Li(C_6F_5)$ yields the anion **63**, which has two different boron environments.

Both **62** and the triphenylcarbenium salt of **63** function as cocatalysts for propylene polymerization by $Me_2Si(2\text{-}MeInd)_2ZrMe_2$ [184].

Another type of bimetallic activator is produced when bis(trimethylstannyl) compounds like $1,2\text{-}C_6H_4(SnMe_3)_2$ are allowed to react with alkylaluminum chlorides (Fig. 28). Catalysts derived from $Cp_2TiMeCl$ and the bis(alkylaluminum) complexes show significantly higher activities than when $AlMeCl_2$ is the cocatalyst [185].

The relative effect of MAO and boron-based anions on polymerization performance was the focus of two papers. Propylene polymerization with $Me_2Si(Flu)(N\text{-}t\text{-}$

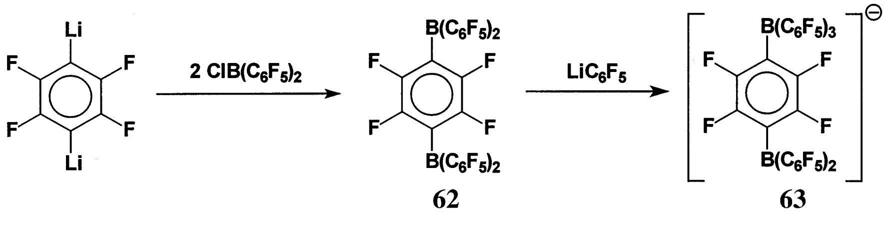


Fig. 27. Synthesis of binuclear boron activators.

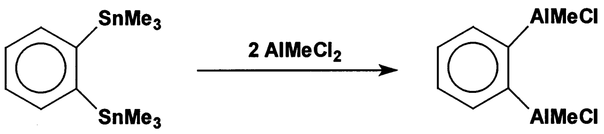


Fig. 28. Synthesis of binuclear aluminum activator.

Bu)ZrX$_2$ (X = Cl, NMe$_2$) produces acetone soluble oligomers when MAO is the cocatalyst, but a variety of products ranging from fractions soluble in acetone at − 10°C to fractions insoluble in refluxing acetone are formed when Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] is used [186]. Propylene polymerization by a mixture of *rac*- and *meso*-Me$_2$Si(2,3,5-Me$_3$Cp)$_2$ZrCl$_2$ shows that the polymerization activity decreases in the order of cocatalysts Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] > MAO > AlEt$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]. Both boron-based cocatalysts give greater fractions of atactic polymer than does the MAO-cocatalyzed system; the reasons are not clear [187]. In EPDM production, it was found that the cocatalyst mixture Al(*i*-Bu)$_3$-Li[B(C$_6$F$_5$)$_4$]–B(C$_6$F$_5$)$_3$ was more effective in generating polymerization-stable catalysts than MAO (unacceptable excess required), [Ct][B(C$_6$F$_5$)$_4$] or B(C$_6$F$_5$)$_3$ alone (short-lived high activity), or Li[B(C$_6$F$_5$)$_4$] alone (inactive) [188].

Comparing alkylaluminums in the catalyst system Cp$'_2$ZrCl$_2$–AlR$_3$–B(C$_6$F$_5$)$_3$ indicates that catalyst activity decreases in the order AlMe$_3$ > Al(*i*-Bu)$_3$ > AlEt$_3$ ≪ AlEt$_2$Cl for Et(Ind)$_2$ZrCl$_2$ and Al(*i*-Bu)$_3$ > AlMe$_3$ ≪ AlEt$_3$ for Cp$_2$ZrCl$_2$ [189]. There are optimum levels of aluminum alkyl, however, with excessive amounts (above 300–400:1) suppressing catalyst activity.

16. Structural and theoretical studies

Part of the attraction of single-site catalysts to chemists is that, unlike conventional Ziegler–Natta systems, they are quite amenable to comprehensive characterization and make an excellent basis for theoretical studies on the process by which chain growth occurs. Many disclosures detail the interaction of metal component and cocatalyst, as well as computational examinations on the effect the catalyst structure has on olefin insertion.

When (1,3-(SiMe$_3$)$_2$C$_5$H$_3$)Zr(η^3-allyl)(η^4-2,3-dimethylbutadiene) is allowed to react with B(C$_6$F$_5$)$_3$, a zwitterionic bis(allyl) complex is formed which was structurally characterized [190]. In a toluene diluent, this complex acts as a single component catalyst for ethylene polymerization. The chemistry of (1,3-(SiMe$_3$)$_2$C$_5$H$_3$)ZrMe(η^4-2,3-dimethylbutadiene) is somewhat different. This compound undergoes slow loss of methane to form a binuclear complex [(1,3-(SiMe$_3$)$_2$C$_5$H$_3$)Zr(μ_2-η^1:η^4-2,3-Me$_2$C$_4$H$_3$)]$_2$. Only one of the butadienyl units is reactive even in the presence of an excess of B(C$_6$F$_5$)$_3$, forming a binuclear zwitterion. This too polymerizes ethylene, though at a slower rate than either the methyl precursor or the allyl complex (Fig. 29) [191].

Alkyl complexes of $Cp(1,3\text{-}(t\text{-}Bu)_2Cp)MR_2$ are unreactive toward $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ when $R = CH_2Ph$ or neophyl, but when R = Me, cationic complexes are formed [192]. These exhibit low polymerization activity toward ethylene, attributed to the steric bulk of the substituted cyclopentadienide. In the presence of one equivalent of $B(C_6F_5)_3$, the zirconium dimethyl complex forms the cation, which is unstable at elevated temperatures, decomposing to a 'tuck-in' cation. A dimeric cation is detected when two equivalents of zirconocene dimethyl are added to the boron activator (Fig. 30).

The formation of a 'tuck-in' cationic metallocene is not limited to *t*-butyl-substituted cyclopentadienides. When $(Me_2NCMe_2Cp)_2ZrMe_2$ is allowed to react with $B(C_6F_5)_3$, an unstable monomethyl cation is generated. This intramolecularly eliminates methane to produce a *spiro*-metallocene cation (Fig. 31) [193]. The authors postulate that this C–H activation may figure in the chain-growth process, perhaps as a chain-transfer reaction.

The products from the reaction of $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiR_2$ with $B(C_6F_5)_3$ depend on the alkyl group. When R = Me, the cationic monomethyl complex, a polymerization catalyst, is formed. In the presence of excess metal dimethyl, the dimer $[\{Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe\}_2(\mu\text{-}Me)]^+$ exists in equilibrium with the mononuclear cation and dimethyl complex. When $R = CH_2Ph$, intramolecular

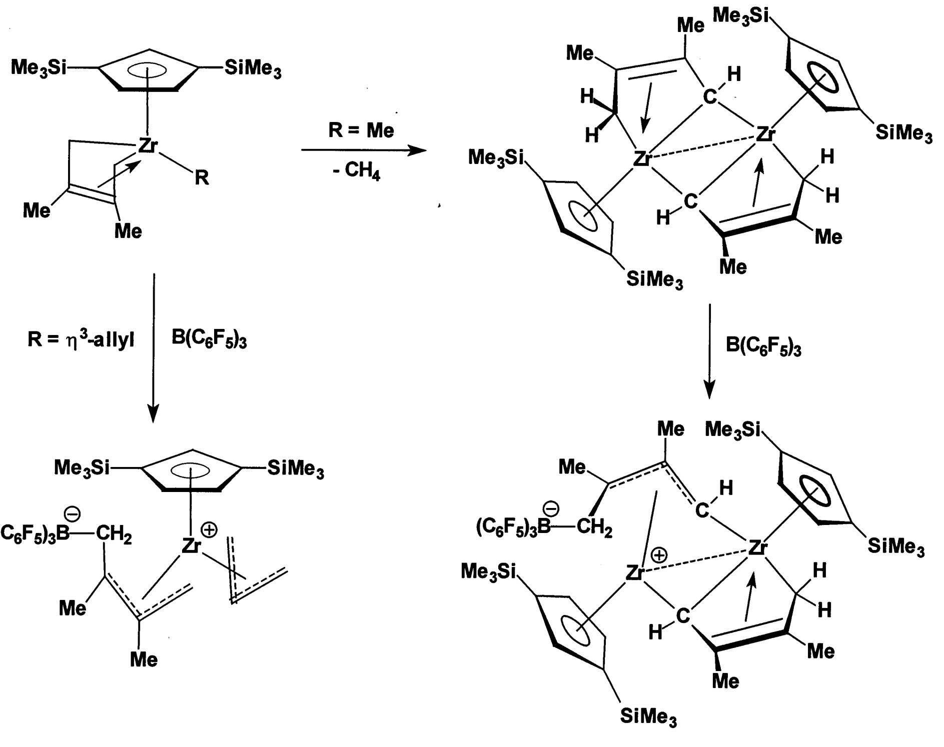


Fig. 29. Reactions of $(C_5H_3(SiMe_3)_2)Zr(2,3\text{-butadiene})$ complexes.

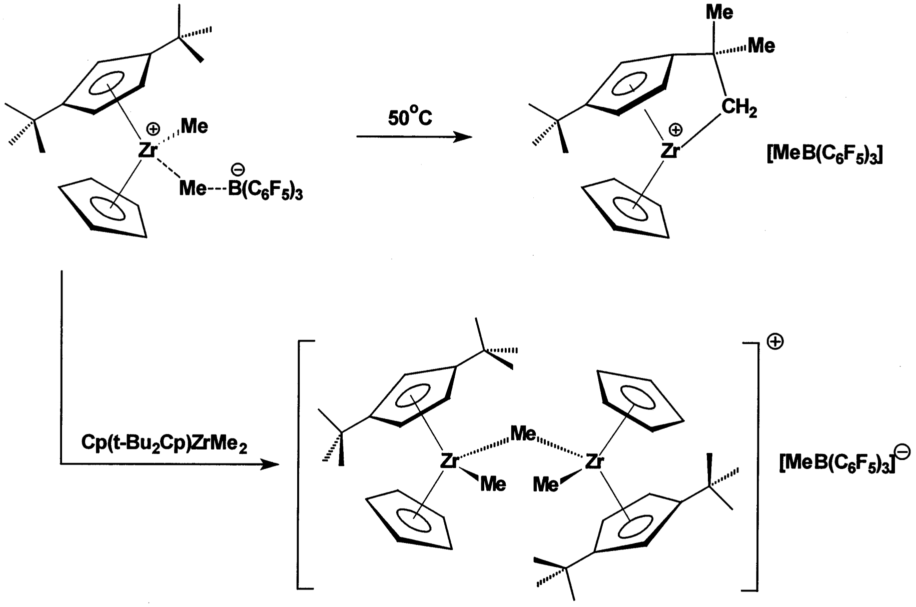


Fig. 30. Reactions of ((*t*-Bu)$_2$Cp)(Cp)ZrMe(μ-Me)(B(C$_6$F$_5$)$_3$)

elimination of toluene occurs to afford the μ-methylene cation, which is polymerization-inert (Fig. 32) [194].

When the ‘tuck-in’ complex Cp*(C$_5$Me$_4$CH$_2$)ZrPh is allowed to react with HB(C$_6$F$_5$)$_2$ the boron compound adds to the methylene group to give a product chelated by a pendant hydridoborate group. This complex acts as a polymerization catalyst in the presence of MAO, but activities are rather low (Fig. 33) [195]. The action of B(C$_6$F$_5$)$_3$ affords a zwitterionic compound in which the fluoroaryl group stabilizes the cationic zirconium atom. This compound also polymerizes ethylene either as a single-component catalyst [196] or when cocatalyzed by MAO.

When B(C$_6$F$_5$)$_3$ is allowed to react with bis(cyclopentadienyl)(butadiene) complexes of hafnium and zirconium, a zwitterionic complex is formed. For less-substituted rings, the ortho fluorines of the B(C$_6$F$_5$)$_3$ group interact with the cationic metal center (Fig. 34). This is a dynamic process, with all six *ortho*-F groups

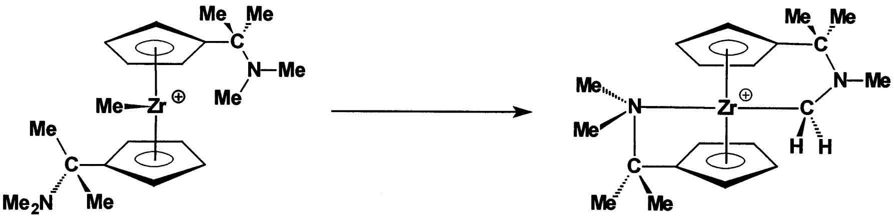


Fig. 31. Metalation of (C$_5$H$_4$(CMe$_2$NMe$_2$)ZrMe$^+$.

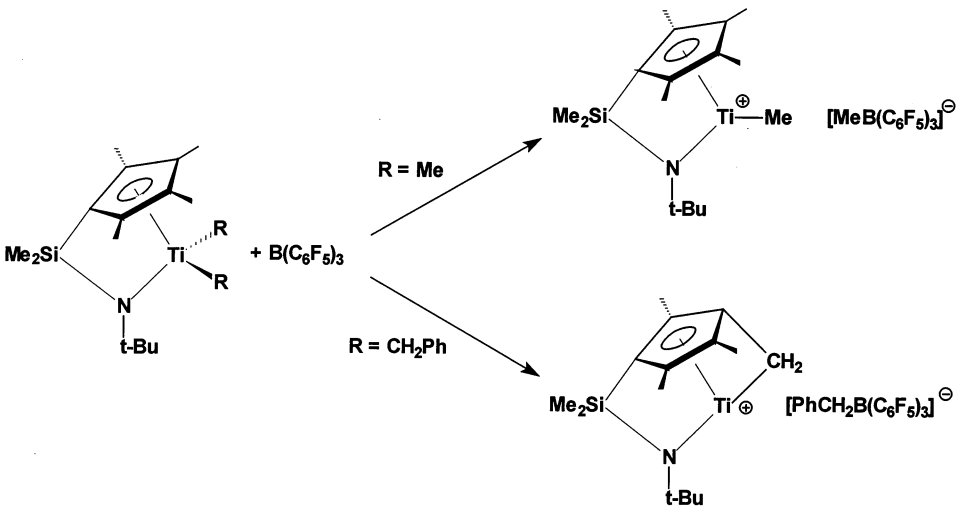


Fig. 32. Reactions of $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiR_2$ with $B(C_6F_5)_3$.

becoming equivalent at about 240 K [197]. Reaction of these complexes with methylenecyclopropane affords the regioisomeric insertion products, which exhibit a π-interaction of the internal olefin with the metal [198]. The more sterically constrained complex $Cp^*_2Zr(\eta^4\text{-}C_4H_6)$ gives an 'open' zwitterion on reaction with $B(C_6F_5)_3$; the X-ray crystal structure indicates no C···F···M interaction. This

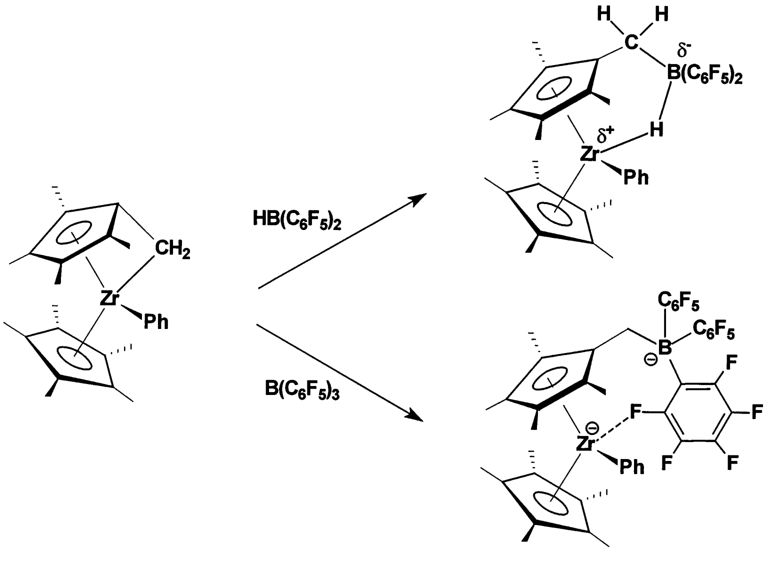


Fig. 33. Reactions of $Cp^*(C_5Me_4)(\mu\text{-}CH_2)ZrPh$ with boron activators.

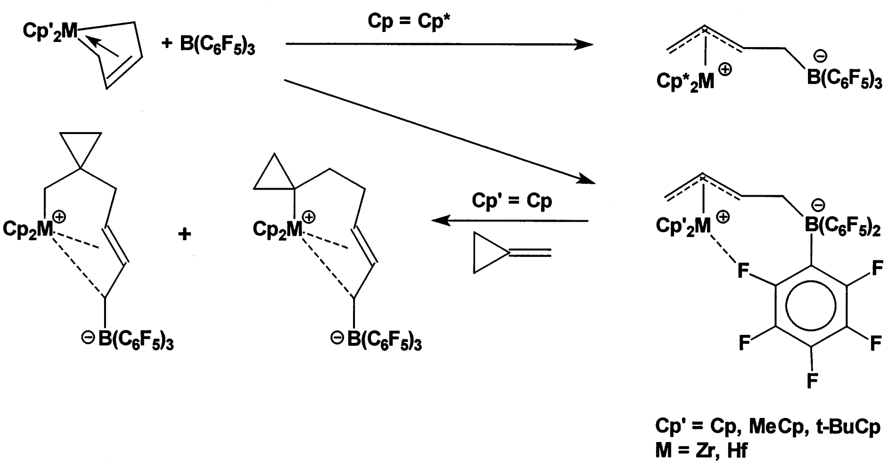


Fig. 34. Reactions of Cp'_2Zr(butadiene) with $B(C_6F_5)_3$.

compound functions as a single-component catalyst for the homopolymerization of ethylene or propylene [199].

$B(C_6F_5)_3$ abstracts a methyl group from Cp^*TiMe_3 to form $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, which is stable below 0°C. Despite the electrophilic nature of the metal center, isotopic labeling of the methyl groups indicates that no α-agostic interactions are present. In the presence of additional Cp^*TiMe_3, an unstable dimeric cation $[(Cp^*TiMe_2)_2(\mu\text{-}Me)][MeB(C_6F_5)_3]$ can be observed by NMR [200]. Replacing one of the methyl groups in the precursor trimethyl complex with $-C_6F_5$ or $-OC_6F_5$ affords $Cp^*TiMe(X)(\mu\text{-}Me)B(C_6F_5)_3$ on reaction with $B(C_6F_5)_3$ [201]. The $-C_6F_5$ derivative dissociates neither into ion pairs nor the neutral precursors, while the anion in the $-OC_6F_5$ complex dissociates more easily. All three titanium complexes function as polymerization catalysts, giving polypropylene with molecular weights above 10^6.

The interaction of metallocenes with MAO—an indeterminate mixture of partially hydrolyzed $AlMe_3$—has long been an area of conjecture, though the generation of an ion-pair complex has now been generally accepted. Tritto and co-workers compared the ^1H- and ^{13}C-NMR spectra of $Cp_2Zr(^{13}CH_3)_2$–MAO with those of the enriched metallocene activated by $AlMe_3$ or $B(C_6F_5)_3$. From these, the presence of $[Cp_2Zr(^{13}CH_3)][MeMAO]$, $[(Cp_2Zr(^{13}CH_3))_2(\mu\text{-}^{13}CH_3)][MeMAO]$ and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2][MeMAO]$ were deduced [202].

These same investigators examined the course of ethylene polymerization by $Cp_2Ti(^{13}CH_3)Cl$–MAO to determine the contribution of the carbene species $Cp_2Ti{=}^{13}CH_2$ to the process. Exposure of the catalyst solution to isotopically enriched ethylene showed a decrease in intensity of the cationic metallocene complex, but no change in the concentration of the alkylidene complex [203]. In the oligomerization of norbornene, insertion of the olefin into the $Cp_2Ti(^{13}CH_3)^+$ cation takes place at 0°C without contribution by the alkylidene complex, but at

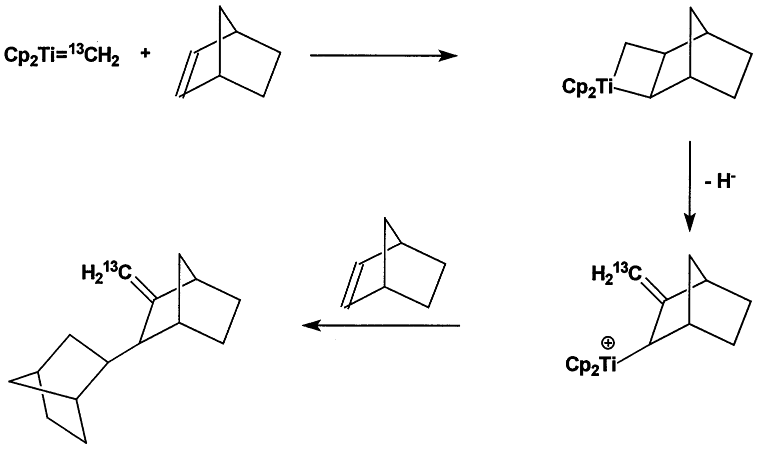


Fig. 35. Norbornene dimerization by $Cp_2Ti{=}^{13}CH_2$.

20°C, a methylidene norbornane dimer is formed. This was attributed to participation by the titanium carbene without ring opening taking place (Fig. 35).

By analyzing the methane evolved from the reaction of Cp'_2ZrX_2 ($X = Cl$, Me) with deuterated MAO in protio- or deuterotoluene, a mechanism for methane evolution was proposed. This involves attack by the Cp_2ZrMe^+ cation on a Cp_2ZrMeX group and loss of methane to form $[Cp_2ZrMe(\mu_2\text{-}\eta^5{:}\eta^1\text{-}Cp)ZrMeCp]^+$ (Fig. 36) [204]. The production of more than one equivalent of methane per zirconium indicates a restoration of Zr–Me groups.

A DFT (density funtional theory) calculation on the $Cp_2TiMeCl{-}AlMe_2Cl$ catalyst in ethylene polymerization examined not only the ethylene insertion reaction, but how the $[AlMe_2Cl_2]^-$ counterion affected the process. The energetically most favorable process is one in which the Cp_2TiMe^+ active species is not completely separated from the anion, but one in which an olefin-separated ion pair $Cp_2TiMe^+/C_2H_4/AlMe_2Cl_2^-$ collapses back to a $Cp_2Ti(C_3H_7){-}Cl{-}AlMe_2Cl$ product after olefin insertion [205]. Methylalumoxane was deemed to be a superior cocatalyst to $AlMe_3$ for $Cp_2TiMeCl$ and $Cp_2ZrMeCl$ because of the tricoordinate oxygen atoms exerting an electron-withdrawing effect on the aluminum centers, rendering them more acidic. Dispersion of the negative charge over the alumoxane framework also plays a part in favorable insertion thermodynamics [206].

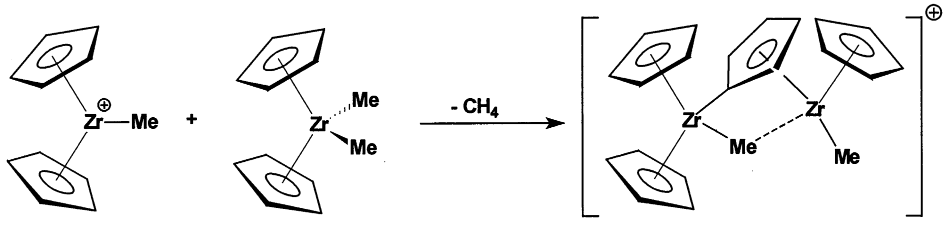


Fig. 36. Postulated mechanism for methane loss in Cp_2ZrX_2–MAO catalysts.

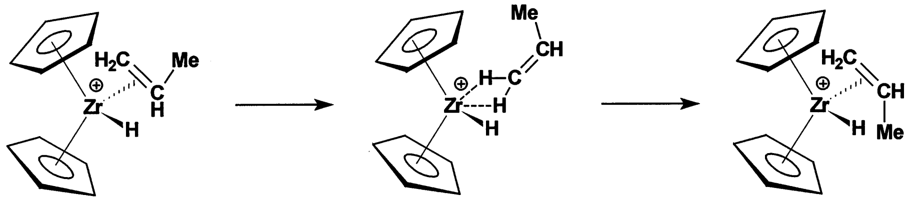


Fig. 37. Olefin rotation in $Cp_2ZrH(H_2C{=}CHCMe)^+$.

The PM3(tm) method has been found wanting for optimizing transient structures and transition states in ethylene polymerization by Cp_2ZrMe^+ or $CpCr(H_2O)Me^+$, though a hybrid method using gradient-modified DFT and PM3(tm) gave a more accurate estimate of the barrier for monomer insertion [207]. A theoretical study of a variety of d^0 methyl metal complexes and their reaction with ethylene indicates that ligands *trans* to coordinated ethylene inhibit insertion; bis(cyclopentadienyl)titanium and zirconium methyl cations have no such geometry and are predicted to perform well as catalysts [208].

Stereo- and regioerrors in propylene polymerization serve to depress the melting point of the resultant polymer. One explanation of the origin of these errors is that there is a isomerization of the alkyl chain. A DFT study of the mechanisms of this isomerization concludes that it is best explained by β-H transfer from the alkyl chain, olefin rotation, and subsequent reinsertion. The change of coordinated enantioface may occur through the CH_2 terminus of the coordinated olefin (Fig. 37) [209]. A molecular mechanics study and comparison to experimental results of the regioselectivity of chiral *ansa*-metallocenes shows that 'open' metallocenes like $Me_2C(Ind)_2ZrCl_2$, which have relatively low stereospecificity, are largely regiospecific while more sterically constrained metallocenes like $Et(4,7\text{-}Me_2Ind)_2ZrCl_2$ lead to a higher number of 2,1 and 3,1 placements [210]. Aspecific and syndiospecific catalysts are far more regiospecific than isospecific catalysts, a phenomenon attributed to the 'wrong' enantioface of the monomer preferring a secondary insertion in isospecific catalysts while for aspecific and syndiospecific catalysts, the activation barrier to primary insertion is much lower than that for secondary insertions [211].

Having determined that symmetry-based predictions of stereospecificity in metallocenes, especially for C_1-symmetric complexes, is inadequate, Fink and co-workers have developed a new model which examines the lowest-energy conformers and determines energy levels through molecular mechanics calculations [212]. Using this method, they predicted that $Me_2C(3\text{-}i\text{-}PrCp)(Flu)ZrCl_2$ should function as a hemi-isotactic catalyst, an assertion later confirmed experimentally.

$H_2Si(Cp)(NH)Ti{-}R^+$ (R = ethyl, propyl) was used as the model to examine chain termination and long-chain branching in 'constrained-geometry' catalysts. β-Hydrogen transfer to monomer is energetically favored over β-hydrogen transfer or C–H σ-bond metathesis. An unusual mechanism for introducing long-chain branching by σ-bond methathesis (Fig. 38) was deemed less favorable energetically to the conventional model of reincoroporation of α-olefin macromers [213].

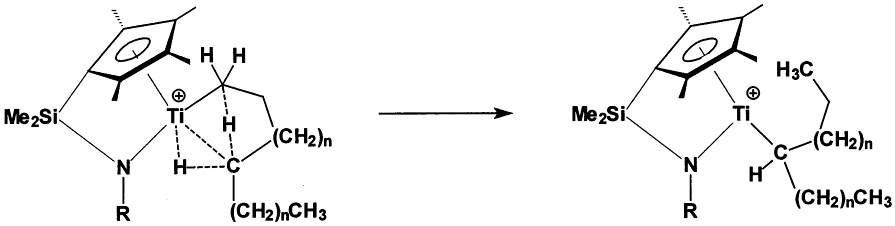


Fig. 38. σ-Bond methathesis mechanism for long chain branching.

Examining chelating alkoxide complexes of titanium and zirconium using density functional methods shows that the activation barrier for ethylene insertion is lower for titanium. The sulfur bridge interacts strongly with the metal center, stabilizing the cationic center over complexes with methylene bridges or those where the aryl groups are directly bridged. The transition from a γ-agostic state after ethylene insertion to a β-agostic state (Fig. 39) is more exothermic for the titanium complex, possibly explaining why the insertion barrier is lower [214].

The activation energies for $Cp(PH_3)M(CH_2CH_2)H^+$ were calculated to be 0.3 kcal mol^{-1} for Co, 2.7 for Rh, and 6.1 for Ir. The insertion reaction is exothermic for cobalt and rhodium (− 3.4 and − 1.0 kcal mol^{-1}), but endothermic for iridium (+3.7 kcal mol^{-1}). The insertion of ethylene into $Cp(PH_3)MMe^+$ has a higher activation barrier, but is exothermic for all three metals. The cobalt complex is known to have a β-agostic interaction, but the interaction weakens on going to rhodium and iridium analogues [215].

Both Ziegler and Morokuma have reported results from density functional studies on ethylene polymerization by $(HN{=}CH{-}CH{=}NH)MMe^+$ (M = Ni, Pd) [216]. These catalysts are known to produce branched homopolyethylene, but there is some divergence of opinion about the mechanism for chain isomerization: Morokuma proposes that the $[L_2M(CH_2CH_2CH_3)]^+$ complex proceeds by a hydride-olefin species $[L_2MH(H_2C{=}CH{=}CH_3)]^+$, the olefin of which rotates and reinserts to form $[L_2M(CH(CH_3)_2]^+$. Ziegler suggests that the abstraction and rotation are part of a concerted process. Calculations on the larger molecule

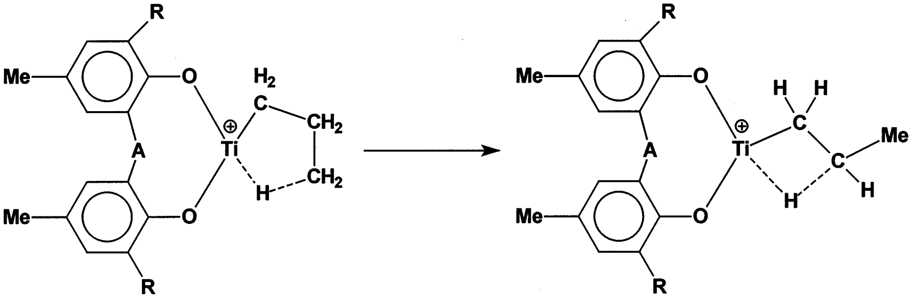


Fig. 39. γ-Agostic to β-agostic interaction in titanium bis(phenolate) catalysts.

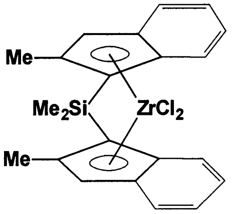
(ArN=Cme–CMe=Ar)NiMe$^+$ (Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$) were carried out using a combination of molecular mechanics (for the ligand set) and quantum mechanics (for the active site). This allowed a more accurate assessment of activation barriers for propagation, isomerization, and termination [217].

17. Polymerization and copolymerizations of ethylene

Single-site catalysts find special value in the copolymerization of ethylene with a variety of α-olefins. The high reactivity of these catalysts toward α-olefins makes accessible resins of much lower densities than those produced from conventional Ziegler–Natta systems. The narrow compositional distribution and random incorporation of comonomer improves mechanical and optical properties while reducing extractable fractions. Novel polymer structures are also possible: supported Et(Ind)$_2$ZrCl$_2$–MAO or Me$_2$Si(C$_5$Me$_4$)(N-t-Bu)TiMe$_2$–B(C$_6$F$_5$)$_3$ catalysts are reported to copolymerize ethylene and 1-hexene in such a manner that the polymer fraction with higher comonomer content occurs in the higher molecular weight portion of the copolymer [218], opposite to that seen in conventional Ziegler–Natta catalysts, which produce low-molecular weight, non-crystalline fractions.

Metallocene complexes with fused ring substituents (substituted indenyl and fluorenyl) attracted interest as procatalysts for ethylene polymerization and copolymerization.

Bis(indenyl) complexes of the general formula (R$_n$C$_9$H$_{8-n}$)CpZrCl$_2$ (R = Me, Ph; $n = 1–3$) are more active and produce polymers of higher molecular weight than Cp$_2$ZrCl$_2$ [219]. Substituting the cyclopentadienyl ring has an adverse effect and (1-MeO–(CH$_2$)$_2$–Ind)CpZrCl$_2$ is only feebly active, probably due to intramolecular coordination of the methoxy group to the cationic metal site. While *rac*-Me$_2$Si(2-MeInd)$_2$ZrCl$_2$ finds value in isotactic propylene polymerization, the *meso* isomer **64** has an application in ethylene–octene copolymerizations.



64

In cases where [1-octene] ≪ [ethylene], copolymers with [EO] and [OE] dyads totaling 96% and low levels of [EE] and [OO] placements indicates an almost alternating copolymer [220]. This was rationalized in terms of the comonomer coordination in the different steric environments (fused-ring and methyl-bearing sides) of the molecule. Mülhaupt and co-workers examined the effect of ligand substitution on ethylene-1-octene copolymerizations using Me$_2$Si(Ind′)$_2$ZrCl$_2$–MAO catalysts (Table 3) [221]. Polymers from the 2-methyl derivatives exhibit

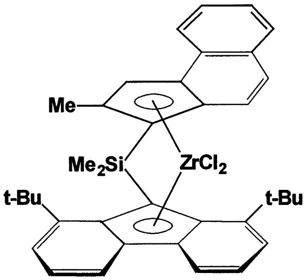
Table 3
Ethylene–octene copolymerization with $Me_2Si(Ind')_2ZrCl_2$–MAO catalysts

Catalyst	Activity[a]	MW ($\times 10^{-3}$)	C_2 content (mol%)	C_8 content (mol%)	r_E	r_O	r_Er_O
$Me_2Si(Ind)_2ZrCl_2$	1598	90.8	88.2	11.8	18.9	0.014	0.27
$Me_2Si(2\text{-}MeInd)_2ZrCl_2$	894	140	88.6	11.4	19.5	0.013	0.25
$Me_2Si(Benz[e]Ind)_2ZrCl_2$	1667	77.7	80.6	19.4	10.7	0.076	0.81
$Me_2Si(2\text{-}Me\text{–}Benz[e]Ind)_2ZrCl_2$	596	172	77.8	22.2	10.1	0.118	1.20

[a] Mole inserted monomer units/(mole l^{-1} total monomer concentration $\times$ mol metallocene $\times$ time) $= 10^{-3}$.

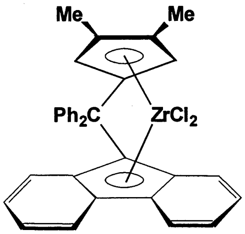
higher molecular weights, while those from benzo derivatives are more octene rich. The activation barriers to octene insertion were calculated to be lower for the benzo derivatives, so octene insertion is more favorable and a more random copolymer is formed.

The fluorenyl-based metallocenes exhibit superior activity and, where tested, comonomer incorporation than their less substituted counterparts. Thus compound **65** produces ethylene–octene copolymer with higher molecular weight and lower density at higher activity than $Me_2Si(Ind)(Flu)ZrCl_2$ [222].



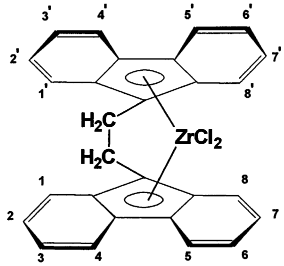
65

Compound **66** incorporates more 1-hexene than $(1,3\text{-}Me_2Cp)_2ZrCl_2$, produces a much higher molecular weight polymer than $Me_2C(Cp)(Flu)ZrCl_2$ and has a much higher catalyst activity than either [223].



66

The effect of substitution in $Et(Flu)_2ZrCl_2$ **67** is not clear (Table 4).



67

For example, *t*-butyl groups in the 2- and 7-positions improve activity over $Et(Flu)_2ZrCl_2$, but methyl or ethyl groups in the same remote locations depress

Table 4
Ethylene polymerization by 1,2-Et(Flu′)(Flu′)$ZrCl_2$

(Flu′)(Flu″)	Activity (kg $mmol^{-1}$ Zr·h^{-1})	MW ($\times 10^{-3}$)
(4,5-dimethylfluorenyl)$_2$	2601	444
(4-methylfluorenyl)$_2$	2408	610
(4,5-dimethylfluorenyl)(fluorenyl)	1965	240
(4-benzylfluorenyl)$_2$	1464	610
(3,4-benzofluorenyl)(fluorenyl)	941	430
(2,7-dinaphthylfluorenyl)(fluorenyl)	693	760
(2,7-dinaphthylfluorenyl)$_2$	666	270
(2,7-di-*t*-butylfluorenyl)$_2$	613	93
(4-benzylfluorenyl)(fluorenyl)	561	510
(4,5-benzofluorenyl)$_2$	485	570
(fluorenyl)$_2$ (reference)	420	620
(2-naphthylfluorenyl)$_2$	375	620
(4,5-benzofluorenyl)(fluorenyl)	279	1050
(1-methylfluorenyl)$_2$	221	270
(2-methylfluorenyl)$_2$	217	610
(2,7-dimethylfluorenyl)$_2$	214	680
(1,8-dimethylfluorenyl)(fluorenyl)	210	200
(2,7-diethylfluorenyl)$_2$	189	830
(2,7-dimethylfluorenyl)(fluorenyl)	125	575

activity. Methyl groups in the 4- and 5-positions lead to a 5-fold increase in activity over the reference metallocene [224].

‘Constrained-geometry’ catalysts such as $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$ are known to produce VLDPE and elastomers of high molecular weight. Another study has found that complexes containing amide groups with primary carbon atoms (e.g. $Me_2Si(C_5Me_4)(N\text{-}n\text{-}octyl)TiCl_2$) or secondary carbon atoms (e.g. $Me_2Si(C_5Me_4)(N\text{-}c\text{-}C_{12}H_{23})TiCl_2$) in combination with MAO give higher comonomer incorporation than the *t*-butyl derivative [225].

Karol and co-workers studied a variety of factors and their consequences in ethylene copolymerizations using metallocene catalysts [226]. Catalyst activities and comonomer reactivity increase with increasing MAO concentrations; this was attributed to a greater degree of ion separation. The activity and copolymerizing activity of the catalyst is strongly dependent on the ring substituents, with $Ph_2C(Cp)(Flu)ZrCl_2$ and $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ incorporating the most comonomer, $(n\text{-}BuCp)_2ZrCl_2$ and $(Ind)_2ZrCl_2$ the most active, and $Me_2Si(Cp)_2ZrCl_2$ the least active. A surprising variance in chain ends was also observed with different catalysts—vinyl, produced from chain elimination after ethylene insertion, was predominantly formed from $Me_2Si(Cp)_2ZrCl_2$; vinylidene groups, produced by elimination after 1,2 α-olefin insertion was predominatly formed from $(Ind)_2ZrCl_2$; and vinylene groups, produced by chain elimination after 2,1 α-olefin insertion was predominantly formed from $Ph_2C(Cp)(Flu)ZrCl_2$ (Fig. 40). In ethylene homopolymerizations, vinylene groups are produced, although their concentration falls as ethylene pressure is increased. An isomerization reaction

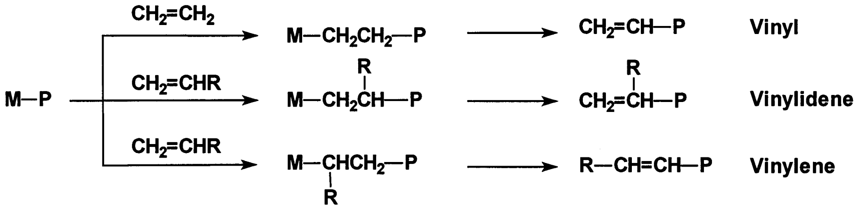


Fig. 40. Mechanisms for formation of chain-end olefin structures.

involving β-hydride elimination, followed by chain isomerization, reinsertion, and a second β-hydride elimination was deemed the most likely pathway (Fig. 41) [227].

Comparing the performance of Et(Ind)$_2$ZrCl$_2$ and Et(Ind)$_2$HfCl$_2$ with MAO in the copolymerization of ethylene and propylene or 1-octene shows that higher molecular weight copolymers with less crystallinity (resembling homogeneous vanadium catalysts) are formed from the hafnocene [228]. Catalyst activities are accelerated for these catalysts on addition of propylene to approximately 20–50 mol% in the feed stream. Above and below these limits, the polymer becomes more crystalline and diffusion of comonomer into the insoluble polymer more difficult [229]. Et(CH(i-Pr)$_3$)(NMe$_2$)TiCl$_2$–MAO catalysts produce ethylene–propylene copolymers with concentrations of head-to-head sequences lying between those from homogeneous vanadium catalysts and those from metallocene catalysts [230].

Ethylene-α-olefin-diene terpolymers prepared from (1,3-Me$_2$Cp)$_2$ZrCl$_2$–MAO catalysts have lower surface roughness and better shape retention than those produced from a conventional VO(OEt)Cl$_2$–Al$_2$Et$_3$Cl$_3$ catalyst [231]. Comparing Et(Ind)$_2$ZrCl$_2$ and Et(Ind)HfCl$_2$ in the terpolymerization of ethylene, propylene, and ethylidene norbornene reveals the hafnocene to be less active than the zirconocene, but forming polymers of higher molecular weight with more comonomer.

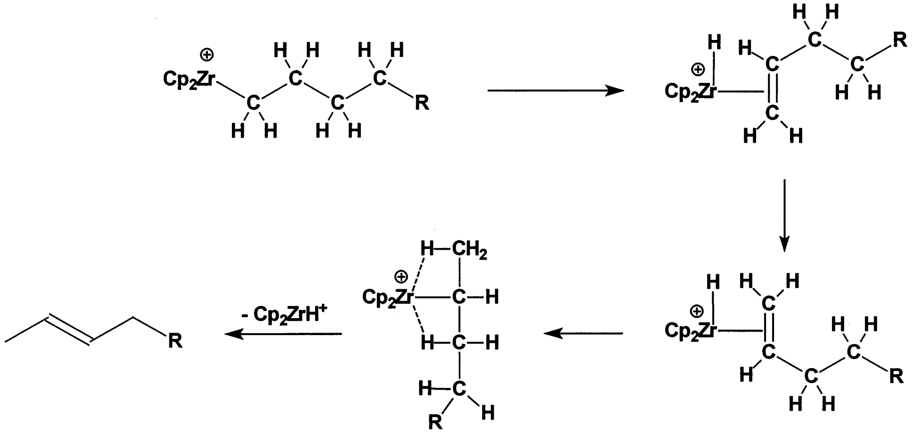


Fig. 41. Mechanism for vinylene chain-end formation by metallocene catalysts.

The EPDM from metallocene catalysts shows less crystallinity and a lower glass transition temperature than that from a conventional vanadium catalyst [232].

Mono(cyclopentadienyl) titanium complexes like $Et(C_5H(i\text{-}Pr)_3)(NMe_2)TiCl_2$–MAO [233] and $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2–B(C_6F_5)_3$ [234] were used to terpolymerize ethylene, propylene, 1-octene, or styrene, and dienes like ethylidene norbornene and α,ω-dienes. The functionality can be used subsequently for vulcanization. The process may be carried out at temperatures above 100°C using $Cp^*Ti(N(SiMe_3)_2)Me_2$ with MAO or $[HNMe_2Ph][B(C_6F_5)_4]$; an unsubstituted cyclopentadienyl ligand affords polymers of lower molecular weight at lower activities [235].

Using Cp_2ZrCl_2–MAO to copolymerize ethylene with propylene, 1-butene, 1-hexene, or 1-octene shows the usual rate enhancement and a lowering of polymer melting point on increasing the length of the short-chain branch, even though the comonomer composition remains constant [236]. Incresing the pressure in a $Et(Ind)_2ZrCl_2$–MAO catalyst for ethylene–hexene copolymerization increases the productivity of the catalyst (g polymer mol^{-1} catalyst) but decreases somewhat the activity of the system (g polymer mol^{-1} catalyst·bar); the crystallinity and melting point of the copolymer increase as the ethylene pressure is increased as well [237]. Increasing the temperature of an ethylene-1-octene copolymerization catalyzed by $Me_2Si(2\text{-}Me–Benz[e]Ind)_2ZrCl_2$–MAO catalyst while keeping the ethylene–octene molar ratio constant leads to lower molecular weights and lower octene incorporation. Increasing the temperature while keeping the ethylene pressure and octene concentration constant affords lower molecular weight copolymers of relatively uniform composition. These results were explained in terms of the solubility of ethylene in the toluene diluent employed [238].

Low molecular weight homo- and copolymers ($MW = 10\ 000$), useful as adhesive components and viscosity modifiers, are prepared from $(n\text{-}BuCp)_2ZrCl_2–Al(i\text{-}Bu)_3–[HNMe_2Ph][B(C_6F_5)_4]$ catalysts at high temperatures and pressures (260°C, 1500 bar) with high hydrogen concentrations in the feed stream [239]. The copolymers can also be prepared from $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$ or $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)Ti(\eta^4\text{-}1,3\text{-pentadiene})$ and $B(C_6F_5)_3$ [240]; a hydrogen:ethylene mol% ratio over 1 is needed to achieve the desired low molecular weight.

Ethylene–styrene copolymers are accessible using single-site catalysts and recently Dow has commercialized these resins under the name Index™. A 'constrained-geometry' catalyst like $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$ best accomodates the large styrene or methylstyrene monomer incorporating them more efficiently than $Et(Ind)_2ZrCl_2$ [241]. The zirconocene complex has a marked preference for ethylene insertion over styrene insertion, but $Me_2C(Cp)(Flu)ZrCl_2$ is more reactive toward styrene, producing a low crystallinity alternating copolymer [242].

The behavior of a series of $Me_2Si(Cp')(N\text{-}R)MCl_2$–MAO catalysts in ethylene-styrene copolymerizations is summarized in Table 5. The fluorenyl zirconium complex affords the highest molecular weight at the cost of low styrene incorporation while $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$ appears to give the best balance of activity, molecular weight, and styrene incorporation [243].

Table 5
Ethylene–styrene copolymerization by mono(cyclopentadienyl)amide catalysts

Catalyst	Activity (kg mol^{-1} Ti·h^{-1}·mol l^{-1})	Styrene content (mol%)	T_m (°C)	Mn ($\times 10^{-3}$)
$Me_2Si(C_5Me_4)$(N-*t*-Bu)$TiCl_2$	3074	15.8		53
Me_2Si(Ind)(N-*t*-Bu)$TiCl_2$	435	20.5	118.0	11
$Me_2Si(3\text{-}Me_3Si\text{–}Ind)$(N-*t*-Bu)$TiCl_2$	255	5.7	92.9	38
Me_2Si(Flu)(N-*t*-Bu)$ZrCl_2$	194	1.1	124.0	121
$Me_2Si(C_5Me_4)(N\text{–}CH_2Ph)TiCl_2$	38	26.0	122.7	12
Me_2Si(Ind)(N-*t*-Bu)$TiCl_2$	25	53		4

The Ti(III) complex $Et(C_5Me_4)(NBu_2)TiCl_2$ has a catalyst activity equivalent to $Me_2Si(C_5Me_4)$(N-*t*-Bu)$TiCl_2$, while affording a polymer with higher molecular weight (180 000 vs. 82 000) and higher styrene incorporation (6.3 vs. 4.2 mol%) [244]. Polymerizing ethylene and styrene with a $Cp^*Ti(OPh)_3$–MAO catalyst produces mixtures of copolymer and ethylene and styrene homopolymers. The extent to which these components are formed is dependent on reaction conditions: copolymer formation is favored between 40–60°C and at Al:Ti between 300 and 1000. Higher or lower temperatures, higher Al:Ti ratios, or addition of $AlMe_3$ promotes homopolymer formation [245].

Comparing the performance of linked bis(phenolate) titanium complexes (**39**) in ethylene–styrene copolymerization, Okuda and co-workers found that while thio-bridged complexes had the highest catalyst activity (80–110 kg mol^{-1} Ti·h^{-1}), the ethylene-bridged compound incorporated high levels of styrene; copolymers with as much as 36 mol% styrene were accessible. A relatively more accessible active site with this ligand was deemed the key [246].

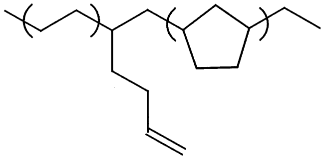
Ethylene and styrene may be terpolymerized with comonomers such as 1-octene, 1,5-hexadiene (which cyclopolymerizes), and norbornene; a $Me_2Si(C_5Me_4)$(N-*t*-Bu)$TiCl_2$–MAO catalyst was used [247]. Styrene by itself inhibits catalyst activity while 1-octene by itself increases activity. In combination, the catalyst activity goes through a maximum with increasing styrene concentration. A ^{13}C-NMR analysis of the polymer indicates no styrene–octene dyads. Elastomeric interpolymers of ethylene, styrene, and 4-ethylidene-8-methyl-1,7-nonadiene optionally copolymerized with propylene or 1-octene—formed from a $Me_2Si(C_5Me_4)$(N-*t*-Bu)$TiCl_2$–MAO catalyst—vulcanize faster and have higher heat stability than ethylidenenorbornene-containing elastomers [248].

Copolymerizing ethylene and *p*-methylstyrene using metallocene catalysts affords ethylene-*p*-methylstyrene copolymers which can be functionalized or metalated with butyllithium to form initiators for the anionic polymerization of styrene or methyl methacrylate (Fig. 42) [249].

Some quite unusual comonomers are amenable to polymerization by single-site catalysts. A $(n\text{-}BuCp)_2ZrCl_2$–MAO catalyst terpolymerizes ethylene, 1-pentene, and

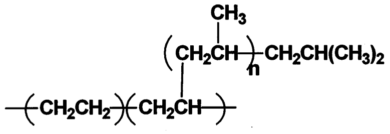
1-butene, 1-hexene, or 1-octene to a polymer reported to have superior properties to the ethylene copolymers [250]. Adding 1,2-polybutadiene to a ethylene-1-octene copolymerization catalyzed by $Et(C_5Me_4)(NMe_2)TiCl_2–AlEt_3–[Ph_3C][B(C_6F_5)_4]$ system results in a broadening of MWD and MFR; this controllable breadth of MWD may assist in processibility of the polymer [251]. Isobutylene and 2-methyl-1-butene, not normally reactive with coordination catalysts, are copolymerized with ethylene by a $Me_2Si(C_5Me_4)(N\text{-}c\text{-}C_{12}H_{23})TiMe_2–[Ph_3C][B(C_6F_5)_4]$ catalyst to poly(ethylene-co-isobutene) containing as much as 45 mol% IB [252].

Copolymerization of ethylene and 1,5-hexadiene using a $Me_2Si(H_4–Ind)_2ZrCl_2$–MAO catalyst at high-pressure (1500 bar), high-temperature (180°C) [253] or more moderate conditions using a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO catalyst [254] affords polymers containing both 1-hexenyl branches and 1,3-cyclopentane rings, caused by incorporation of both olefin functionalities (**68**); the concentration of vinyl groups increases with increasing comonomer concentration.



68

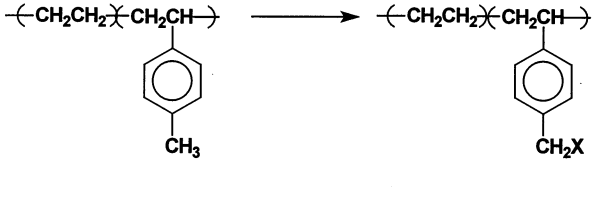
Atactic polypropylene macromers—prepared from a $Cp^*_2ZrCl_2$–MAO catalyst—are incorporated to as much as 5 mol% by a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO catalyst (**69**).



$$-\!\!\left(CH_2CH_2\right)\!\!\left(CH_2\underset{\left(CH_2\overset{CH_3}{\overset{|}{C}H}\right)_n CH_2CH(CH_3)_2}{CH}\right)\!\!-$$

69

In these macromers *n* averages 11, but the chain length does not appear to affect the extent of incorporation [255].



X = SiMe$_3$, PS, Br, PMMA, COOH

Fig. 42. Functionalization of ethylene-4-methylstyrene copolymers.

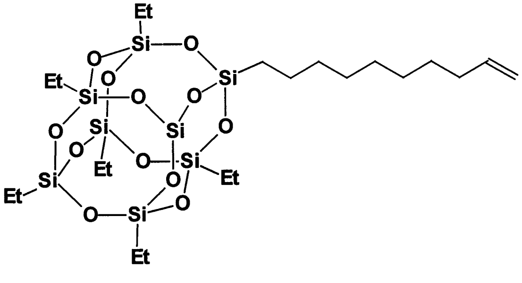
1,3-Butadiene is incorporated into ethylene chains with a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO catalyst with mostly *trans*-1,4 and some 1,2-placements; no *cis*-1,4 placements were detected [256]. 4-Methyl-1,3-pentadiene is incorporated into ethylene chains with a $CpTiCl_3$–MAO catalyst with 1,2 or 1,4 arrangements despite the fact that the homopolymerization always gives syndiotactic-1,2 polymers. This was attributed to a lack of unsaturation in the penultimate group of the growing chain; vinyl coordination appears to favor 1,2 placements [257].

Incorporating polar monomers into the ethylene chain remains a desired goal in olefin polymerization catalysis. Unfortunately, the electrophilic active site is frequently deactivated by lone pairs of electrons on the comonomer. Efforts to produce new resins containing functional groups continues using single-site catalysts.

Copolymerization of ethylene with alcohols (1,1-methyl-2-propen-1-ol, 5-hexen-1-ol, 10-undecen-1-ol), acids (10-undecenoic acid), and esters (methyl-9-decenoate) using a $(n\text{-}BuCp)_2ZrCl_2$–MAO catalyst gave the best conversion of monomer and lowest decline in catalyst activity when 10-undecen-1-ol was the comonomer [258]. 1,1-Methyl-2-propen-1-ol is not incorporated at all, owing to the proximity of the alcohol functionality to the metal and the steric constraints exerted by the geminal methyl groups. The activity of an $Et(Ind)_2ZrCl_2$–MAO catalyst for ethylene-propylene copolymerization is approximately halved in the presence of 11-chloroundec-1-ene termonomer; the shorter chain 5-chloro-1-pentene suppresses activity completely [259].

It is not clear that adding bulky substituents to the polar atom improves catalyst performance. When ethylene is copolymerized with *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene using a $Me_2Si(Benz[e]Ind)_2ZrCl_2$–MAO catalyst, the activity declines by almost 90% as the comonomer:metal ratio increases from 3600 to 7200 [260]. However, the polymerization performance of a $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$–$B(C_6F_5)_3$ catalyst in ethylene–octene copolymerization appears to be little affected by the presence of 4-allyl-2,6-di-*t*-butylphenol, which is randomly incorporated in the copolymer chain [261]. The oxidation state of the metal may also be a factor: The $Et(C_5(i\text{-}Pr)_3H)(NMe_2)TiCl_2$–MAO catalyst incorporates 5-norbornene-2-carboxaldehyde some 4 times more efficiently than a Cp'_2MCl_2–MAO system [262].

The unusual silasesquioxane monomer **70** can be incorporated to about 1 mol% in polyethylene using Cp_2ZrCl_2, $Me_2Si(Ind)_2ZrCl_2$, or $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiCl_2$ complexes with MAO [263].

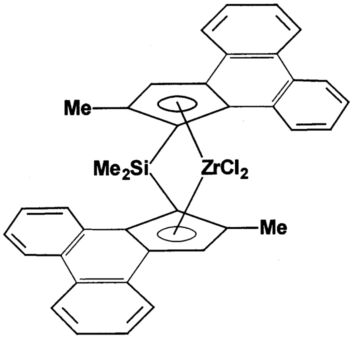


70

The copolymer has a melting point some 7–18°C lower than that of homopolyethylene and exhibits somewhat greater thermostability in air.

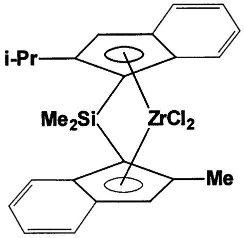
18. Polymerization of propylene and higher α-olefins

Efforts continue to raise the melting point of isotactic polypropylene prepared from metallocene catalysts. In the presence of MAO, the 2-methyl cyclopenta[l]phenanthryl complex **71** polymerizes propylene with extremely high activities (56 kg mmol^{-1} Zr·h^{-1}) to *i*-PP with over 97% mmmm pentads [264].



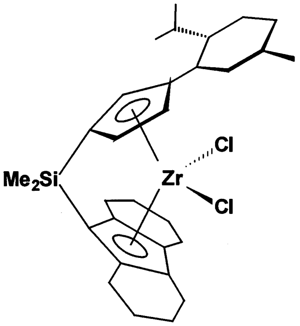
71

However, the presence of regioirregularities (0.4%) reduces the melting point to 152°C. It has been suggested that asymmetric *ansa* metallocenes like **72**, one indenyl group bearing a secondary- or tertiary-carbon substituent in the 2-position, has higher isospecificity and regiospecificity than 2-methylindenyl compounds or even symmetric 2-isopropylindenyl) metallocenes [265].



72

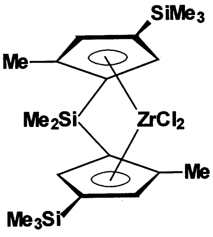
The C_1-symmetric (3-menthyl-Cp)(octahydrofluorenyl) complex **73** affords polypropylene 80–90% mmmm pentads versus 35–65% for Me$_2$Si(3-menthyl-Cp)(C$_5$Me$_4$)ZrCl$_2$ [266].



73

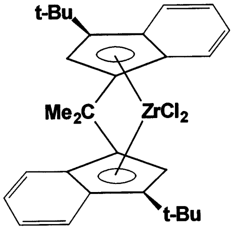
This was attributed to the greater lateral expanse of the octahydrofluorenyl ligand (6.76 Å) over the tetramethylcyclopentadienyl ligand (5.18 Å).

Ewen has suggested that ideal metallocenes for stereospecific α-olefin polymerization bear substituents at the β position for stereodirection and substituents at the α position to 'lock' the polymer chain into a specific conformation [267]. An example is **74**.



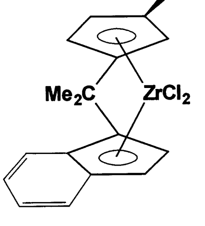
74

Polypropylene from the *rac*-isopropylidene(3-*t*-butyl–Indenyl)zirconium compound **75** has surprisingly high isotacticity (mmmm = 94.8%) when one considers that the 3-methylindenyl analogue is almost aspecific [268].



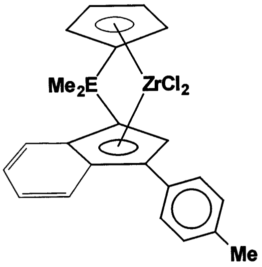
75

The catalyst is sensitive to propylene concentration: at low monomer concentrations, chain epimerization is relatively rapid and the isotacticity of the polymer falls accordingly (mmmm = 53.5%). Oddly, the C_1-symmetric compound *threo*-Me_2C(3-*t*-BuCp)(3-*t*-BuInd)$ZrCl_2$ exhibits much less dependence on propylene pressure, with mmmm falling from 99.5% at 4.0 atm propylene pressure just to 95.6% at 0.5 atm [269]. Me_2C(3-*t*-BuCp)(Ind)$ZrCl_2$ polymerizes propylene to low-molecular weight products, with the *threo* isomer (**76**) affording isotactic material, while a-PP is formed from the *erythro* isomer [270].



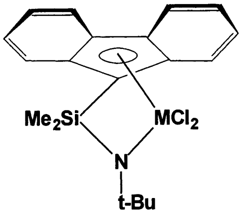
76

Weak syndiospecificity (rr = 0.48) is exhibited by the polypropylene produced from the *ansa*-3-*p*-tolyl–Indenyl complex **77** (E = C, Si) while the 2-substituted isomer is almost totally aspecific [271].



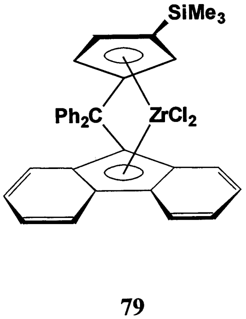
77

In the case of the fluorenyl amide compounds (**78**), when M = Ti, a syndiotactic-enriched polymer is formed (rr = 0.6, rrrr = 0.38) by chain-end control as calculated from Bernoullian statistical equations [272].



78

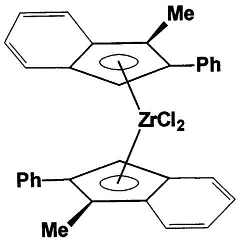
When M = Zr, atactic regioregular polypropylene is produce [273]; less regioregular polypropylenes are formed from tetramethylcyclopentadienyl- or indenyl-amide titanium catalysts. The methylene-bridged trimethylsilylcyclopentadienyl complex **79** is reported to produce polypropylene with both isotactic (mmmm = 33.8%) and syndiotactic (rrrr = 46.5%) blocks [274].



79

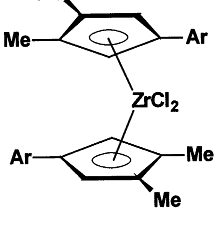
At low temperatures (− 40 to 0°C), a $Cp^{*}TiMe_3$–$B(C_6F_5)_3$ catalyst polymerizes propylene to tough, elastomeric atactic polypropylene with narrow MWD (1.1) and high molecular weight ($MW = 6–40 \times 10^5$) [275]. Adding small amounts of $AlMe_3$ inhibits activity and broadens the MWD to nearly 10, though no alkylaluminum adducts were detected by NMR. When these $Cp'TiCl_3$ complexes (Cp′ = Cp, Cp*, Ind, heptamethylindenyl) are supported on $MgCl_2$ and activated by Al(*i*-Bu)$_3$, 7 to 50% of the polymer is heptane insoluble, the best results being with Me_7Ind. On adding five to eight equivalents per titanium of a monoester like ethyl benzoate as an external donor, heptane insolubles as high as 93% and isospecificities (% mmmm) as high as 94% can be achieved at the cost of catalyst activity [276].

Elastomeric polypropylene containing isotactic and atactic blocks are prepared from 'oscillating' catalysts such as (2-Ph–Ind)$_2$ZrCl$_2$. Hafnocene analogues afford polymers with considerably shorter isotactic blocks, with mmmm = 8–9 versus 25–35% for the zirconocenes. The rotational frequency of the two catalysts is similar (6700–6800 Hz), so the disparity in isotacticity is due to the slower propagation rate of the hafnocene catalyst [277]. Polymerizing propylene with (2-Ph–Ind)$_2$ZrCl$_2$–MAO in liquid propylene at − 2 to 10°C yields polymer with a melting point of 140°C, comparable to that produced from Et(Ind)$_2$ZrCl$_2$–MAO [278]. (1-Me-2-Ph–Ind)$_2$ZrCl$_2$ complexes (**80**) can be isolated and crystallographically characterized in both *rac* and *meso* diastereomers.



80

The methyl group serves to twist the phenyl ring out of essential planarity with the indenyl ring, increasing dihedral angle from 10–12 to 26–33°. With MAO, the complex affords essentially atactic polymer (%m = 55–60) of lower molecular weight and at much lower productivities than (2-Ph–Ind)$_2$ZrCl$_2$ [279]. The 1-aryl-3,4-dimethyl complexes **81** (Ar = Ph, *p*-tolyl, 2-naphthyl) also lead to atactic polymers [280].



81

Examining the enantioselectivity of the first propylene insertion into a $Me_2Si(Ind')_2ZrCl_2$ compound cocatalyzed by ^{13}C-labeled MAO reveals the surprising result that catalysts with Ind′ = benzoindenyl and 2-methylbenzoindenyl afford highly isotactic polypropylene (mmmm = 93%), but the enantioselectivity of the first insertion is quite poor ([e] = 0.54). In contrast, when Ind′ = indenyl, the isotacticity is relatively poor (mmmm = 78%), but the enantioselectivity is rather better ([e] = 0.60) [281]. These results were duplicated when 3-methyl-1-pentene was used as the monomer [282] and reinforce the view that the purpose of the stereorigid ligand set is not to direct the monomer, but to fix the configuration of the polymer chain, which influences the enantioselectivity of the incoming monomer.

Looking at variables other than the metal component, adding hydrogen to an *ansa*-zirconocene–MAO catalyst system leads to an increase in catalyst activity and decrease in polymer molecular weight, but no effect on the stereoselectivity of the catalyst. While it is tempting to attribute the rise in activity to the activation of a 'resting' catalyst after a 2,1 monomer insertion, end-group analysis does not support this hypothesis [283].

An $Et(Ind)_2ZrCl_2$–MAO catalyst has a maximum activity at 60°C at an Al:Zr ratio of 1000 [284]. When $Me_2Si(Benz[e]Ind)_2ZrCl_2$ is the catalyst, the activity reaches its maximum when $[Al] = 20\ mmol\ l^{-1}$ regardless of zirconocene concentration [285]. The cocatalyst influence is only on the kinetics of polymerization: polymer properties—molecular weight, melting point, and microstructure—are unaffected. The case is the same in polypropylene produced under similar conditions from $Me_2Si(Ind)_2ZrMe_2$ using either $[Ph_3C][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_4Si(i\text{-}Pr)_3)_4]$: the former borate salt affords a more active catalyst, but there is no difference in polymer properties [286]. By studying the effect of metallocene concentration, [Al]:[Zr], and temperature on propylene polymerization by a $Et(H_4\text{–}Ind)_2ZrCl_2$–MAO catalyst, a kinetic model was derived, allowing prediction of activity for a given set of polymerization conditions [287].

Comparing homogeneous and supported $Me_2Si(2\text{-}Me\text{–}Benz[e]Ind)_2ZrCl_2$–MAO catalysts, Mülhaupt and co-workers found that the activity of the supported catalyst and the molecular weight and melting point of the *i*-PP formed was lower than that of the homogeneous variant; the percentage of 2,1 insertions was higher. Diffusion effects were held responsible. The supported catalyst also displays less of a behavior dependence with change in temperature [288].

It has also been suggested that shielding a $Me_2Si(2\text{-methyl-4-phenylindenyl})_2ZrCl_2$–MAO catalyst from ≤ 500 nm light improves stability and activity [289]. Carrying out propylene polymerizations under supercritical conditions appears to lead to high activity and polymer bulk densities [290].

Poly(1-butene) prepared from $Et(Ind)_2ZrCl_2$ or $Me_2Si(Ind)_2ZrCl_2$ is somewhat more stereoregular than polypropylene from the same catalysts. The polymer contains no detectible 2,1 placements, save at the chain ends. Instead 4,1 monomer enchainments are detected, indicating that regioirregular insertions lead to a dormant catalyst site which either isomerizes or undergoes elimination [291].

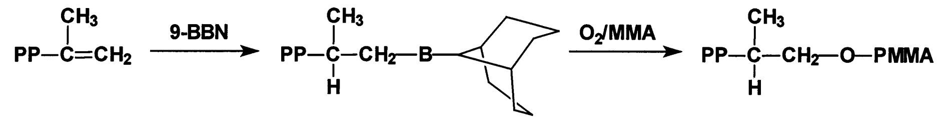
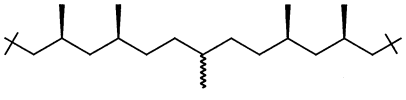


Fig. 43. Graft copolymerization onto metallocene-produced polypropylene.

Propylene can be copolymerized with other olefins to reduce crystallinity and melting points. Propylene-ethylene (4.2 wt% ethylene) copolymers produced from a Et(4,7-Me_2Ind)$_2$ZrCl_2–MAO catalyst have approximately the same amount of structure **82** as the homopolymer has 2,1 placements; the activity increases almost 10-fold.



82

This indicates that ethylene insertion after a regioirregular insertion is competitive with chain elimination and can reactivate sites dormant after 2,1 propylene insertions [292]. Propylene and 1-butene have been copolymerized in a continuous gas-phase process using a silica-supported Me_2Si(2-MeInd)$_2$ZrCl_2–MAO catalyst; the melting point of the polymer is reduced with increasing butene content [293]. The activity of a Et(Ind)$_2$ZrCl_2–MAO catalyst in the copolymerization of propylene and 1-hexene is more drastically affected by changes in alumoxane concentration and adjustments in solvent polarity (by CH_2Cl_2) than is the homopolymerization [294]. Polymer properties are unaffected by the Al:Zr ratio, but addition of dichloromethane increases 1-hexene concentration. Comparing four metallocenes (Me_2Si(Ind)$_2$ZrCl_2, Me_2Si(2-MeInd)$_2$ZrCl_2, Me_2Si(Benz[e]Ind)$_2$ZrCl_2, and Me_2Si(2-MeBenz[e]Ind)$_2$ZrCl_2) in propylene-1-octene copolymerization shows that 2-methylation increased molecular weight and depressed activity while benzannelation improved 1-octene incorporation [295].

Dienes like isoprene, 2-methyl-1,4-pentadiene, and 1,7-octadiene are copolymerized with propylene by a Et(Ind)$_2$ZrCl_2–MAO catalyst. The catalyst activity and polymer melting point are depressed over the homopolymer and, surprisingly, the amount of diene incorporated is not as high as that from a Solvay $TiCl_3$–$AlEt_2Cl$ catalyst [296]. Propylene-1,13-tetradecadiene copolymers prepared from a Me_2Si(Ind)$_2$HfMe_2–[HNMe_2Ph][B(C_6F_5)$_4$] catalyst exhibit superior shear thinning behavior to homopolymer or copolymer produced from a conventional Ziegler–Natta catalyst [297]. 1-Decene-1,7-octadiene copolymers with molecular weights under 20 000 – prepared from a Me_2Si(Ind)$_2$ZrCl_2–MAO catalyst—can be used as viscosity modifiers in lubricants [298].

The olefinic end group of polypropylene formed from a Et(Ind)$_2$ZrCl_2–MAO catalyst can be hydroborated with 9-BBN. The hydroborated polymer can then be used as a radical source to polymerize methylmethacrylate to form a PP–[g]–PMMA copolymer with good efficiency and little broadening of molecular weight distribution (Fig. 43) [299].

The hindered amine 5-*N*,*N*-diisopropylamino-1-pentene can be homopolymerized to an isotactic polymer using metallocene catalysts like $Me_2C(3\text{-}t\text{-}BuCp)(Flu)ZrMe_2$ and $Et(Ind)_2ZrMe_2$ or to syndiotactic polymer using $Me_2C(Cp)(Flu)ZrMe_2$ with $[HNMe_2Ph][B(C_6F_5)_4]$ as a cocatalyst (Fig. 44) [300]. The melting point of the isotactic polymer is as high as 115°C, while the syndiotactic material has a melting point of 110°C.

19. Polymerization of vinyl aromatic olefins

s-PS has enjoyed a rapid development since its discovery in 1985. It combines high heat resistance, chemical inertness, and rapid rate of crystallization. Dow and Idemitsu have begun commercial development of this resin. Mono(cyclopentadienyl) titanium complexes are much preferred procatalysts for syndiospecific styrene polymerization: the $Cp'TiCl_3$–MAO catalysts ($Cp' = Cp$, Ind) afford s-PS with much narrower MWD at 5–10 times the activity of $TiCl_4$ or $Ti(OBu)_4$ [301]. Bis(cyclopentadienyl) metal complexes are inferior catalysts: both Cp_2TiCl_2–Ph_2Zn–MAO [302] and Cp_2ZrCl_2–$AlMe(BHT)_2$ [303] catalysts exhibit low styrene conversions and sizable amounts of ketone-soluble fractions indicative of poor stereoregulating ability.

Cyclopentadienyl titanium complexes containing at least one alkoxide group appear to have superior catalytic performance to $Cp'TiCl_3$ [304]. Thus $CpTiCl_2(OR)$–MAO catalysts have activities double or more that of $CpTiCl_3$ with greater syndiotacticity (90–96 vs. 86.5%) [304a]. Alkoxide-containing catalysts can be generated in situ by reacting $C_5Me_4HSiMe_3$ with $Ti(OR)_3X$ ($X = Cl$, OR) and contacting with MAO or $Al(i\text{-}Bu)_3$–$[HNMe_2Ph][B(C_6F_5)_4]$ [305].

While tetravalent $Cp'TiX_3$ procatalysts are the ones most frequently used, investigators at Dow have found that the trivalent complex $[Cp^*Ti(OMe)_2]_2$ exhibits superior monomer conversion rates to $Cp^*Ti(OMe)_3$ [306]. The trivalent complex $Ti(O_2CN(i\text{-}Pr)_2)_3$ also polymerizes styrene to an s-PP with narrow molecular weight distribution, but monomer conversion is lower than that of a $CpTiCl_3$-based catalyst [307]. DSM's low-valent titanium catalyst $1,2\text{-}Et(C_5Me_4)NMe_2TiCl_2$ in the

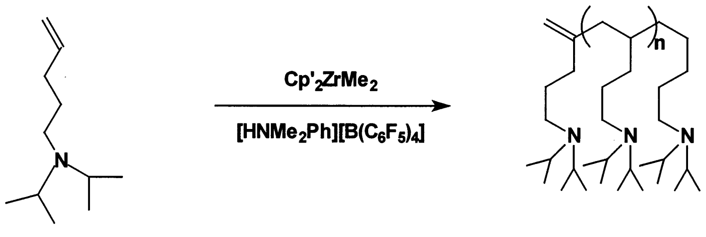


Fig. 44. Synthesis of polar amine copolymer using metallocene catalysts.

presence of MAO produces more stereoregular s-PP at higher activity than $Me_2Si(C_5H_4)(N\text{-}t\text{-}Bu)TiCl_2$–MAO [308].

A number of adjuvants have been suggested to improve catalyst performance. The use of tetraisobutylalumoxane (500 equivalents) to a $Cp^*Ti(OMe)_3$–$Al(i\text{-}Bu)_3$–$[HNMe_2Ph][B(C_6F_5)_4]$ catalyst is claimed to almost double catalyst activity [309]. Adding $SnMe_4$ or $SnPh_4$ to a Cp^*TiCl_3–MAO catalyst system leads to a greater percentage of styrene converted to s-PS [310]. Phenylsilane has a similar beneficial effect on monomer conversion. It acts as a chain transfer agent; like hydrogen, it tends to increase catalyst activity [311]. Treatment of the styrene monomer with dibutylmagnesium removes phenylacetylene and indene impurities, leading to better catalyst performance [312].

An analysis of styrene polymerization by Cp^*TiR_3 ($R = CH_2Ph$, Me) cocatalyzed by MAO, $B(C_6F_5)_3$, or $[Ph_3C][B(C_6F_5)_4]$ indicates that polymerization is first order in monomer, at least at low conversions with chain termination predominantly by β-H elimination [313]. Catalysts with the $[B(C_6F_5)_4]^-$ counterion produce polymers with the highest molecular weight while MAO-based catalysts produce s-PS with lower molecular weight, attributed to the relative coordinating ability of the two anions. Supporting a $CpTiCl_3$–MAO catalyst on silica results in a drop both in activity and syndiospecificity, possibly because the support material has a steric influence on the active catalyst site [314].

Other vinylaromatics as both monomers and comonomers with styrene received some attention in 1997. Semi-crystalline styrene-4-methylstyrene copolymers produced from Cp^*TiX_3–MAO catalysts ($X = Cl$, OMe) have melting points from 245°C at 90 mol% styrene to 220°C at 56 mol% styrene [315]. The non-equilibrium melting points for styrene-4-butylstyrene copolymers prepared from $CpTiCl_3$–MAO declines from 270°C (neat s-PS) to 70°C in a 40 mol% 4-butylstyrene copolymer. The syndiotactic 4-butylstyrene homopolymer melts at 133°C [316]. In contrast, when Cp^*TiCl_3–MAO is the catalyst, an essentially atactic 4-butylstyrene homopolymer is produced [317]. Copolymerizing styrene and (*Z*)-1,3-pentadiene with a $CpTiCl_3$–MAO catalyst affords a copolymer containing syndiotactic 1,2-pentadiene units. The polymer is rather blocky, with substantial amounts of s-PS and s-1,2-pentadiene homodyads and few heterodyads [318]. 4-Vinylpyridine can be polymerized by a $CpTiCl_3$–MAO catalyst to a homopolymer with a melting point of 194°C, but when the monomer is first complexed with $AlEt_3$, the melting point increases to 270°C [319].

In the process for polymerizing styrene by single-site catalysts, it has been found that raising the pressure and temperature in the reactor system improves the activity of a $CpTiCl_3$–MAO catalyst at what appears to be some cost in butanone-soluble product [320]. Styrene is smoothly homopolymerized [321] or copolymerized with divinylbenzene [322] by a Cp^*TiMe_3–MAO–$Al(i\text{-}Bu)_3$ in a corotating twin-screw extruder, the product from which can be fabricated directly from the exit die into a mold or a fiber or film line.

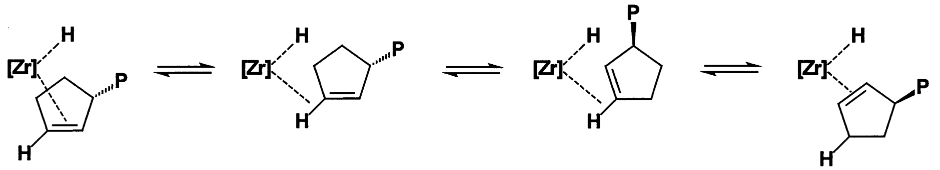


Fig. 45. Isomerization mechanism in cyclic olefin polymerization.

20. Polymerization and copolymerization of cyclic olefins

Poly(cyclopentene) is a highly crystalline polymer with a melting point near 400°C. The material prepared from metallocene catalysts has a 1,3 enchainment of the rings. The presence of *trans*-1,3 units in poly(cyclopentene) prepared from $Et(H_4{-}Ind)_2ZrCl_2{-}MAO$ was determined through kinetic and isotope studies to arise from isomerization without dissociation of the olefin from the metal through a σ-CH complex (Fig. 45) [323]. Very high molecular weight poly(cyclopentene) (melt index = 1) is formed from $(ArN{=}C(R){-}C(R){=}NAr)MCl_2{-}AlEt_3{-}B(C_6F_5)_3$ catalysts ($M = Ni$, Pd, $Ar = 2,6\text{-}(i\text{-}Pr)_2C_6H_3$, $2,6\text{-}Cl_2\text{-}4\text{-}OMeC_6H_2$). The polymers are largely atactic (%m = 50–65) and the crystallinity is quite different than poly(cyclopentene) produced from metallocene catalysts [324].

Copolymers of ethylene and cyclic olefins like norbornene are amorphous resins with glass transition temperatures as high as 250°C. Their stiffness, low creep tendency, and water resistance makes them useful in optical storage media, capacitor films, and medical applications [325]. Single-site catalysts were crucial to achieving the balance of properties and economics essential to commercial development of these resins.

Preferred catalysts for ethylene-cyclic olefin copolymerization are *ansa* metallocenes like $Et(Ind)_2ZrCl_2$ and in particular methylene-bridged fluorenyl complexes like $R_2C(Cp)(Flu)ZrCl_2$; these show the highest activities and, with their relatively open active sites, high comonomer incorporation. In the case of $Me_2C(3\text{-}t\text{-}BuCp)(Flu)ZrCl_2$, the calculated copolymerization ratio r_Er_N for ethylene–norbornene copolymerization is near zero, indicating a highly alternating structure with almost no norbornene–norbornene dyads; near alternating (50:50) E–NB copolymers with melting points of 320°C are formed at high norbornene and low ethylene concentrations [326].

Bergström and Seppälä studied the effect of different polymerization conditions on the properties of ethylene and norbornene produced from a $Et(Ind)_2ZrCl_2$–MAO catalyst, finding that as temperature increased, comonomer conversion and activity improved even as molecular weight suffered. At 70°C, norbornene incorporation drops significantly and the resulting polymers have T_g's below 0°C. Increasing norbornene concentrations adversely affect activity, but polymers with T_g over 150°C can be formed [327]. The norbornene units are relatively isolated, especially at low norbornene levels, but the related catalyst $Me_2Si(Ind)_2ZrCl_2$–MAO forms longer NN blocks [328].

α-Olefin-cyclic olefin copolymers produced from d^0 metallocenes like $Me_2Si(Ind)_2HfMe_2$ or $Me_2Si(C_5Me_4)(N$-*c*-$C_{12}H_{23})TiMe_2$ with $[HNMe_2Ph][B(C_6F_5)_4]$ are rich in comonomer and have narrow molecular weight distributions [329], while ethylene–norbornene copolymer from $Et(C_5H(i\text{-}Pr)_3)(NMe_2)TiCl_2$ has a bimodal molecular weight distribution and two T_g's, one at 15°C, the other at 70°C [330].

Low molecular weight (MW = 5000) propylene copolymers with norbornene, ethylidene norbornene, or dicyclopentadiene produced from metallocene catalysts like $Me_2Si(H_4\text{–}Ind)_2ZrMe_2\text{–}[HNMe_2Ph][B(C_6F_5)_4]$ can be used as tackifier resins in blends with styrene–isoprene–styrene block copolymers, forming adhesives with superior properties to commercial formulations [331].

21. Polymerization of dienes

Mono(cyclopentadienyl) complexes like $CpTiCl_3$ in combination with AlR_3–$[Ph_3C][B(C_6F_5)_4]$ [332] or MAO can polymerize conjugated dienes such as 1,3-butadiene or isoprene. The mechanism by which the polymerization takes place was studied by Extended Hückel Theory. The rate-limiting step is coordination of the monomer to a putative $CpTi^+(\eta^3\text{-R})$ intermediate, resulting in a rearrangement of the growing polymer chain from η^3 to η^1 (Fig. 46). This is an energetically more favorable process for butadiene polymerization than isoprene polymerization. There does not appear to be any significant difference between the two monomers in the insertion step, however [333]. Examining the 1,2 and *cis*-1,4 insertion of butadiene, a molecular mechanics study found the energetic minimum for both processes in a *endo*,*endo* arrangement of monomer and growing chain (Fig. 47) [334].

1,3-Butadiene, 4-methyl-1,3-butadiene, and *cis*- or *trans*-1,3-pentadiene can be copolymerized using a $CpTiCl_3$–MAO catalyst. Polymers with different microstructures were obtained depending on the monomer pairs, with 1,3-butadiene/*trans*-1,3-pentadiene affording alternating to random copolymers, while 1,3-butadiene/4-methyl-1,3-butadiene is blocky. This was interpreted in terms of the most stable coordination modes of the various monomers [335].

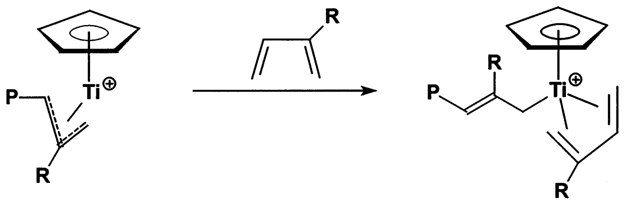


Fig. 46. Rate-limiting coordination of diene by mono(cyclopentadienyl)titanium catalysts.

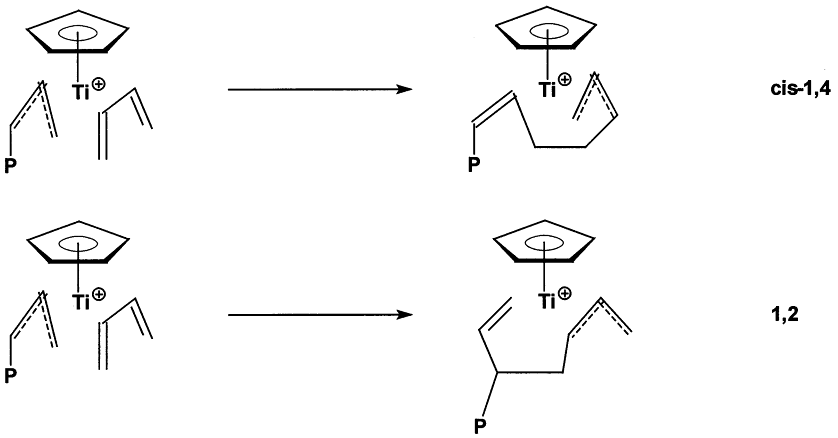


Fig. 47. *cis*-1,4 and 1,2 diene polymerization by *endo,endo* allyl diene titanium complexes.

22. Copolymerization of α-olefins with carbon monoxide

Copolymers of α-olefins and carbon monoxide are now commercially available from Shell under the trade name Carilon. Because of their resistance to heat, moisture, chemicals, and wear, they find applications as plastic gears and fuel tank liners. The alternating copolymers are prepared from catalysts of the late transition metals, in contrast to the random copolymers formed by a free-radical route. Terpolymers of ethylene, propylene, and carbon monoxide are thermoplastic elastomers which can be blended with thermoplastics to improve impact resistance [336].

Palladium complexes with bidentate ligands have been the most common catalysts for alternating olefin–CO copolymerizations, but nickel salts using 1,2-di-2-methoxyphenylphosphinoethane were also successfully used; the catalyst performance was superior to that when 1,2-diphenylphosphinoethane was the ligand or $Pd(OAc)_2$ was the metal source [337]. 1,3-Di-2-methoxyphenylphosphinopropane works well with palladium; 3,3-dimethyl-1-butene can be used as a chain-transfer agent with this catalyst [338]. A Brønsted or Lewis acid is also employed to remove the acetate groups from the metal. $[Bu_4N][BF_4]$ is a relatively ineffective activator while high activity catalysts are formed from triphenylammonium or trimethyloxonium salts [339]. Even though the process is run in methanol, a polar solvent, the relative coordinating ability of the counterion also has a part in catalyst performance; catalysts of the formula $[Pd(dppp)(bipy)][A]_2$ (dppp = 1,3-diphenylphosphinopropane, bipy—2,2′-dipyridyl) are more active when $A^- = [B(C_6F_5)_4]^-$ than when $A^- = PF_6^-$ [340].

A number of other neutral bidentate phosphine ligands have been used with palladium salts in olefin–carbon monoxide copolymer catalysts. Investigators at BP Chemicals used nitrogen-containing phosphines such as $PhP(NEt_2)(CH_2)_3P(NEt_2)Ph$ [341], $R_2P{-}N(Me){-}N(Me){-}PR_2$ (R = Ph, OPh, 2-

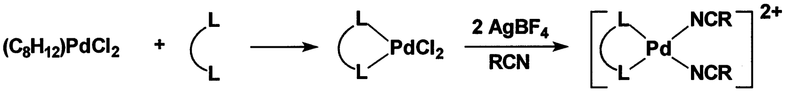


Fig. 48. Generation of olefin–CO copolymerization catalysts.

$MeOC_6H_4$) [342], or $Ph_2P–N(R)–C(=O)–N(R)–PPh_2$ (R = H, Me, Ph) [343]. The catalysts were generated from reaction of the ligand with $[(C_8H_{12})PdCl]_2$ then generating a cation with $AgBF_4$ in the presence of a nitrile (Fig. 48).

Supported catalysts can be prepared by allowing palladium on alumina to react with $[NO][BF_4]$ in an acetonitrile slurry to produce supported $[Pd(CH_3CN)_4][BF_4]_2$. In the presence of 1,3-diphenylphosphinopropane, this supported palladium complex copolymerizes ethylene and CO in slurry or gas-phase processes [344]. Passing an ethylene–carbon monoxide mixture through an acetonitrile solution of $[Pd(CH_3CN)_4][BF_4]_2$ at ambient temperature and pressure before adding phosphine has been reported to improve the ultimate catalyst activity in copolymerization at higher temperature and pressure [345]. The productivity of the process (g g^{-1} M) can be improved by reducing the residence time and increasing the catalyst concentration; activity (g g^{-1} M·h^{-1}) is unaffected [346].

The neutral ligand in these cationic palladium complexes need not be limited to phosphines. $[Pd(bipy)_2][A]_2$ complexes in the presence of [Hbipy][A] ($[A]^- = BF_4^-$, PF_6^-) efficiently copolymerize CO with ethylene or ethylene/propylene mixtures [347]. Bidentate P–O, N–O, and tridentate P–O–N neutral ligands were complexed with Pd(II) precursors to form cationic procatalysts (Fig. 49) [348]. These function as ethylene–CO copolymerization catalysts with the exception of the 2-carbomethoxypyridine complex when $L' = Ph_2PCH_2CO_2Et$.

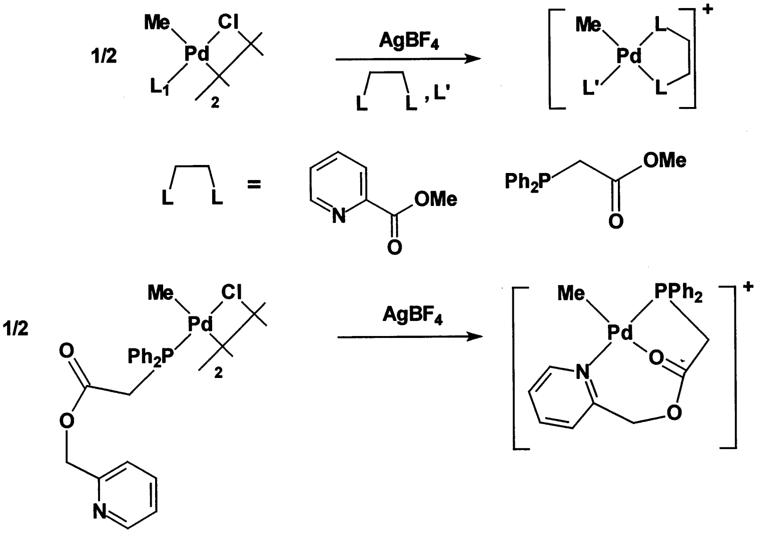
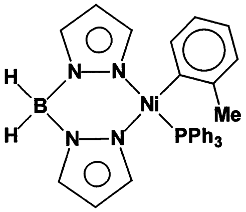
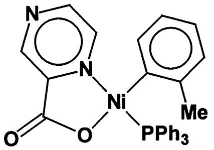


Fig. 49. Generation of cationic Pd(II) complexes for olefin–CO copolymerization.

Monoanionic ligands with nickel and palladium complexes create ‘single-component’ neutral procatalysts for α-olefin–CO copolymerizations. Reaction of $K[H_2B(pz)_2]$ with $NiBr(o\text{-tolyl})(PPh_3)_2$ forms a bis(pyrazolyl) nickel complex **83** which copolymerizes ethylene and CO [349]. The pyrazinecarboxylate complex **84** and the 4-nitro- and 4-methoxypicolinic acid derivatives were also synthesized and tested in ethylene–CO copolymerizations.

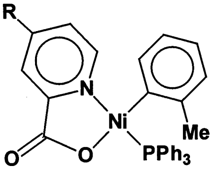


83



84

These SHOP-type catalysts produce alternating copolymers (**85**, $R = NO_2$), polyethylene oligomers (**85**, R = OMe), and non-alternating polyketone [350].

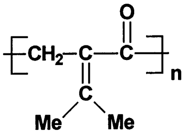


R = NO_2, OMe

85

Carbon monoxide can be copolymerized with 4-vinylcyclohexene using $[Pd(CH_3CN)_4]^{2+}$ in the presence of neutral ancillary ligands (PPh_3, bipy, NPh_3, 1,10-phenanthroline, 2-pyridinecarboxaldehyde butylimine) [351]. 3,3-Dimethylallene is best copolymerized with CO using a $[Pd(PPh_3)(MeCN)_2]^{2+}$ catalyst; bidentate phosphines have an adverse effect on activity.

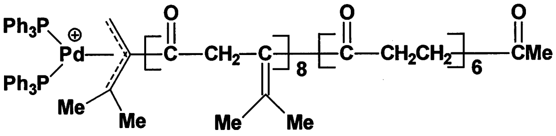
An alternating copolymer (**86**) with pendant isopropylidene groups is formed from the copolymerization of carbon monoxide and 3,3-dimethylallene.



$$\left[CH_2 - \underset{\underset{\underset{Me\quad Me}{C}}{||}}{C} - \overset{\overset{O}{||}}{C} \right]_n$$

86

When ethylene and 3,3-dimethylallene are terpolymerized with carbon monoxide, the polymerization is essentially living and a block copolymer consisting of ethylene-*alt*-CO and dimethylallene-*alt*-CO segments is formed (**87**) [352].



87

23. Supported single-site catalysts

The commercial suitability of single-site catalysts depends in part on their compatibility with current polymerization processes [353]. Processes such as fluidized-bed gas-phase, continuous slurry, and bulk monomer polymerizations almost always employ heterogeneous catalysts. Supported catalysts can even be used in cases when such criteria need not be met, such as solution processes for lower density copolymers. A $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)TiMe_2$–[Ct][$B(C_6F_5)_4$] catalyst supported on 3 μm silica gives a solid suspension which settles very slowly and can be used for in a solution process [354].

Research into immobilizing single-site catalysts on insoluble carriers examines methods of retaining and maximizing catalyst activity while maintaining good particle morphology, narrow particle size distribution, and high product bulk densities without reactor fouling. This research focuses on new carriers, as well as new techniques for combining the metal component, cocatalyst, and support.

Silica remains the carrier of choice for single-site catalysts because of its large surface area and pore volume, chemical inertness, and low cost. Bis(cyclopentadienyl) complexes have the the principal metal procatalyst used, but silica-supported $CpMCl_3$–MAO catalysts exhibit high activities [355] as do Ti(III) complexes like 1,2-Et(C_5Me_4)(NMe_2)$TiCl_2$ [356]. Bis(imido)nickel like (2,3-(2,6-diisopropylphenylimido)butane)nickel dichloride activated by MAO can also be supported on silica and used in slurry [357] or continuous gas-phase processes [358]; the branching for which these catalysts are known is suppressed sufficiently such that the melting point of the polymer is well above the process temperature and no fouling is observed.

The characteristics of the silica appears to have some effect on polymerization performance. A Me_2Si(2-MeBenz[e]indenyl)$_2ZrCl_2$–MAO catalyst supported on acidic silica (pH 5.5) with 15 vol% voids was 2–3 times more active in propylene polymerization than the same catalyst supported on less porous or less acidic silicas [359]. Pretreatment of the silica with $AlMe_3$ removes impurities and increases the propylene polymerization activity of a Me_2Si(2-Me-4-Ph–Ind)$_2ZrCl_2$–MAO catalyst [360]. The same catalyst supported on silica modified by $(MeO)MeSi(CH_2)_3X$

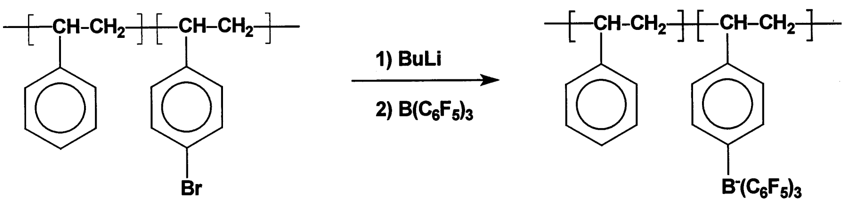


Fig. 50. Synthesis of polymer-bound non-interfering boron anions.

(X = SH or MeO), but activity was vastly diminished when the surface was modified by $(MeO)_3Si-C_6H_4-Cl$ [361].

Because of diffusion effects, the activities and productivities of supported $Et(Ind)_2ZrCl_2$–MAO catalysts are essentially invariant with respect to metallocene loading when porous silicas are used. However the same catalyst supported on non-porous Aerosil exhibits higher activity with higher loading [362]. Studying two supported metallocene catalysts, Fink and co-workers noted that the polymerization behavior of the catalysts varied (induction time and particle fragmentation) as the catalyst was located largely on the catalyst surface or had penetrated into the particle voids [363].

Supported metal complex—MAO catalysts can be prepared by supporting MAO and then allowing it to react with the metallocene, addition of the complex to the support followed by reaction with MAO, or combining the two catalyst components then contacting with the support.

Heat treating MAO to 55–85°C before contacting with the support has been claimed to improve catalyst activity while avoiding reactor fouling. The effect was attributed to the removal of deleterious gels from the alumoxane [364]. Allowing the MAO to react with bisphenol before contacting with the silica was also indicated to have a positive effect on catalyst performance [365]. The metallocene solution may be added to the supported MAO under superatmospheric conditions to improve uniformity of catalyst coating on the support [366].

Silica-supported metallocenes activated by MAO can be prepared from trialkylaluminums hydrolyzed in situ. Adding $AlMe_3$ to silica gel containing adsorbed water in an Al/H_2O ratio less than 1 yields a supported alumoxane which, when contacted with a metallocene, affords a catalyst with reduced fouling tendencies; Al/H_2O ratios greater than 1 increase fouling [367]. Spray-drying a toluene slurry containing silica, $AlMe_3$, and water gives a supported activator for metallocene catalysts [368]; adding a metallocene, $AlMe_3$, and water-saturated nitrogen to a gas-fluidized bed of silica also yields a finished catalyst [369].

Boron-based activating cocatalysts are chemically tethered to a silica support by allowing salts like $[HNMe_2Ph][(C_6F_5)_3B(p\text{-}C_6H_4-OH)]$ to react with silane-modified silicas [370] or $[HNMe_2Ph][(C_6F_5)_3B(p\text{-}C_6F_4-SiCl_3)]$ with silica [371]. The supported cocatalyst can be used with a wide array of bis(cyclopentadienyl) and 'constrained-geometry' metal complexes. Polystyrene has also been used as a support for non-interfering boron anions by allowing poly(styrene-co-*p*-bromostyrene) to react with butyllithium followed by $B(C_6F_5)_3$ (Fig. 50) [372].

Supporting the metal component first, followed by activation, is largely limited to cases in which the metal component is tethered to the support through a bridging group. One motivation for this technique is the perception that the supported catalyst can be leached from the surface. Cp_2ZrX_2 (X = Cl, Me), supported on dehydroxylated silica, was allowed to react with MAO or Al(*i*-Bu)$_3$ in toluene or hexane at 70°C. Both the solids and the supernatant solutions were found to be polymerization active, indicating that desorption of the metallocene from the support had occurred [373].

ICP-AES spectroscopy of Cp_2MCl_2 on modified silica gels indicates that the more extensively the dehydroxylation of the support, the less metallocene is adsorbed. For example, bare silica adsorbs Cp_2ZrCl_2 to the extent of 0.15 mmol g^{-1} SiO_2, while silica dried at 600°C and further reacted with hexamethyldisilazine adsorbed only 0.03 mmol Zr g^{-1} SiO_2. The order of reactivity was $Cp_2HfCl_2 > Cp_2ZrCl_2 > Cp_2TiCl_2$ [374].

The residual hydroxyl groups on silica surfaces have been used to chemically bind the catalyst to the support. Silica substituted with 3-aminopropyl-trimethoxysilane and reacted with $CpTiCl_3$ [375], Cp_2ZrCl_2 [376], or $CpZr(C_5H_4SiMe_2Cl)$ [377] forms a tethered procatalyst, as does $(MeO)_3Si(CH_2)_3Cp$ after deprotonation and reaction with $CpZrCl_3$ (Fig. 51) [378]. (MeO)Me$_2$SiCp′ has been allowed to react with partially dehydroxylated silica and then with $M(NMe_2)_4$ (M = Ti, Zr) or $CpZrCl_3$ to form [silica]–O–SiMe$_2$Cp′M(NMe$_2$)$_3$ or [silica]–O–SiMe$_2$Cp$_2$ZrCl$_2$ [379].

A somewhat longer trisiloxane group with thallium cyclopentadienide and a zirconocene at its termini was allowed to react with *p*-tolylsulfonate-capped silica to produce a tethered metallocene (Fig. 52). Catalyst activity in ethylene polymerization is reduced by 70–80% over the unsupported Cp(Ind)ZrCl$_2$, but polymer properties are otherwise unaffected [380].

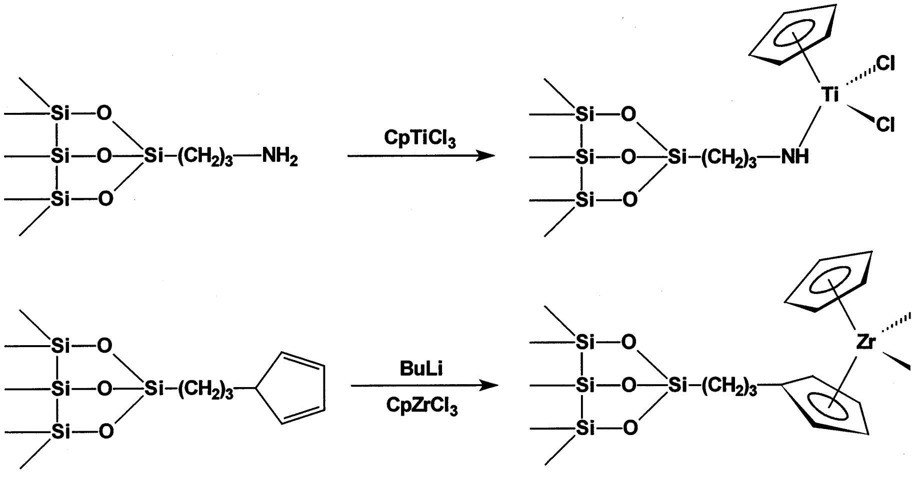


Fig. 51. Synthesis of silica-bound mono- and bis(cyclopentadienyl) metal complexes.

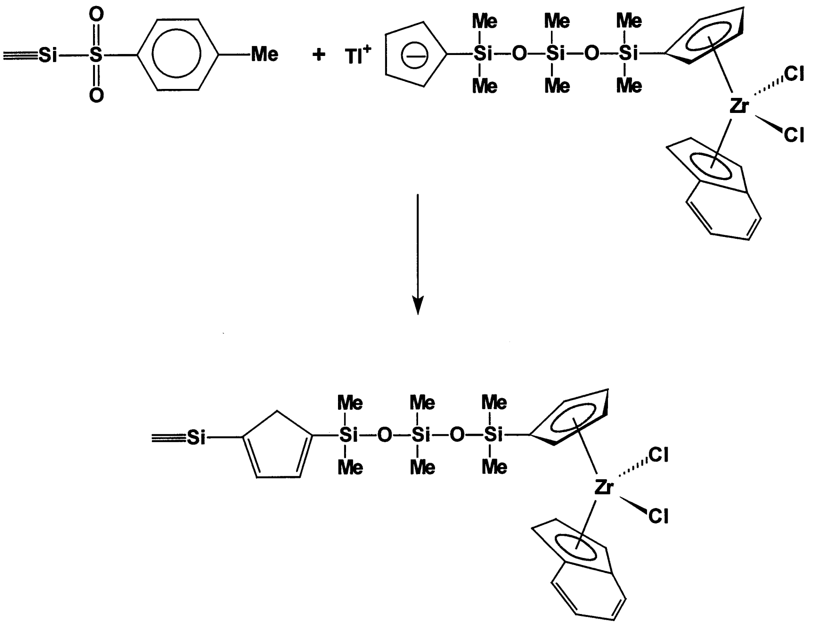


Fig. 52. Synthesis of silica-bound zirconocene catalyst.

Metallocene complexes containing a bridging group can be immobilized on a support through the bridging group. It has been suggested, though not exemplified, that (RO)MeSi(C_5Me_4)(A)MCl_2 complexes (A = N-*t*-Bu, C_5Me_4; M = Ti, Zr) can be bound to silica through the silyl-bridge [381]. ($Cl_3Si(CH_2)_4$)(Me)Si(2-MeInd)$_2ZrCl_2$, prepared from $HSiCl_3$ and ($H_2C{=}CHCH_2CH_2$)(Me)Si(2-MeInd)$_2ZrCl_2$, is claimed to react with partly hydroxylated silica to form a tethered catalyst (Fig. 53) [382]. $Cl_2Si(Ind)_2$, formed from $SiCl_4$ and lithium indenide, can be reacted with lithiated styrene/divinylbenezene copolymer [383], or hydrolyzed to form a polysiloxane polymer [384]. Deprotonation of the polymer-bound ligand and reaction with $ZrCl_4$ also has been claimed to give a supported metallocene catalyst for isospecific α-olefin polymerization.

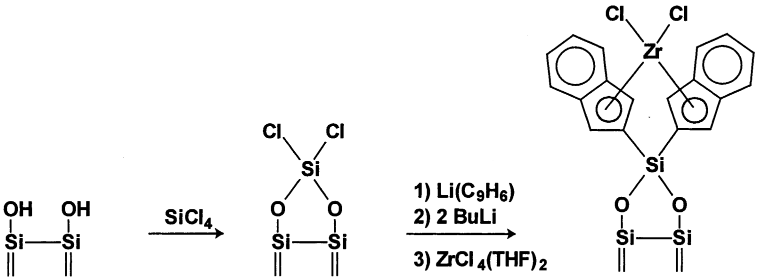


Fig. 53. Preparation of silica-bound *ansa* zirconocene.

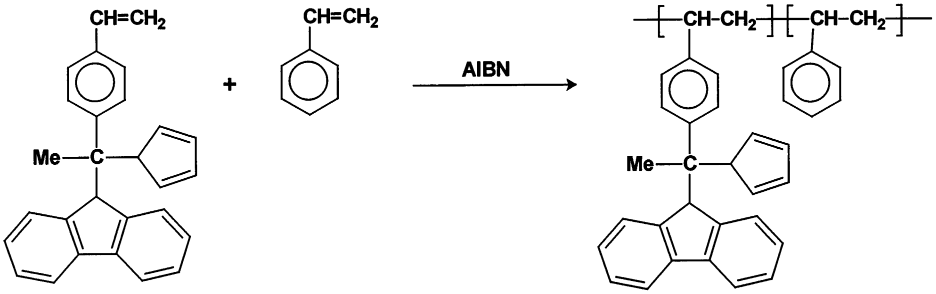


Fig. 54. Polymer-bound ligand for metallocene catalyst.

Syndiospecific propylene polymerization catalysts have been incorporated into polystyrene by copolymerizing styrene with 4-$(C_5H_5)(C_{13}H_9)$(Me)C–C_6H_4–CH=CH_2 (Fig. 54) [385] or into polysiloxanes by hydrolysis of $Cl_2Si(C_5H_5)(C_{13}H_9)$ [386], aromatizing with BuLi, and reacting with $ZrCl_4$.

Metallocene dichlorides and $[HNMe_2Ph][B(C_6F_5)_4]$, cosupported on Al(*i*-Bu)$_3$-treated silica, are activated on the support by aluminum alkyls [387] or BuLi [388] to afford highly active catalysts. Butyllithium may also be used as an adjuvant for supported metallocene–MAO catalysts [389].

Combining the metallocene and MAO before adding to the support appears to be the method of choice for large-scale preparations of supported single-site catalysts. While homogeneous metallocene–MAO catalysts require Al/Me ratios of 1000 or more for high activity, supported catalysts function efficiently at much lower ratios. Supported catalysts with Al/Me ratios under 200 have longer shelf lives than more aluminum-rich catalysts [390]. Allowing a Me_2Si(2-Me-4-Ph–Ind)$_2ZrCl_2$–MAO mixture to stand for 18 h prior to contacting with silica affords a catalyst with over twice the activity of a mixture added to silica without delay [391]. Filtering the metallocene–MAO mixture before combining with the support is claimed to improve activity [392].

Combining the catalyst mixture and the support can be done by spray-drying the mixture in a nitrogen stream heated above the temperature of the least volatile liquid component [393] or using incipient wetness techniques, in which the volume of metal complex–MAO solution is comparable to the pore volume of the support. Volume ratios of 0.6 to 2.5 have been successfully used [394], but for best results the mixture of catalyst solution and support should not form a slurry. An additional prepolymerization step improves particle morphology when a volume of hexane less than or equal to the pore volume of the support is added to the dry catalyst before prepolymerization [395].

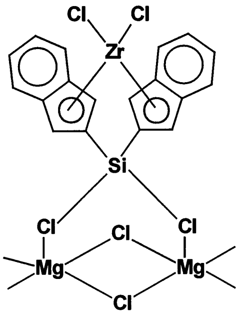
A hybrid technique was used to cosupport two isospecific metallocenes for propylene polymerization. $Me_2Si(H_4$–Ind$)_2ZrCl_2$ was first supported on silica using an incipient wetness method and dried. A Me_2Si(2-MeInd)$_2ZrCl_2$–MAO solution (160% volume of solution/pore volume of support) was then added to the supported first metallocene to produce the finished catalyst. This catalyst had higher activity, less fouling, and better particle morphology to catalysts prepared in a different combination of steps [396].

As an alternative to these techniques, the active catalyst can be assembled in situ by reacting zirconium alkoxides like Zr(O-*n*-Pr)$_4$, the cyclopentadiene derivative, trialkylaluminum, and MAO in the presence of silica. Catalysts active for the slurry or fluidized-bed copolymerization of ethylene and 1-butene were prepared using this method [397].

The effect of catalyst loading was the focus of two disclosures. Reacting Cp_2ZrCl_2 with Davsion 948 silica affords a saturated metallocene loading of about 1 wt%; the surface area is unchanged. $AlMe_3$ is adsorbed to a maximum of about 3 wt% Al, but higher MAO loadings (12 wt%) are possible. While the activity of the Cp_2ZrCl_2–MAO-silica is about 10% that of the homogeneous analogue, the polymer molecular weight is higher. On the other hand, the Cp_2ZrCl_2–$AlMe_3$–silica is active while the homogeneous mixture is not [398]. (1-Me-3-*n*-BuCp)$_2$ZrCl$_2$–MAO catalysts supported on silica show higher activities and higher polymer bulk densities when the loading is kept below about 0.06 mmol Zr g^{-1} support [399].

Research has continued on the suitability of other materials as carriers for single-site catalysts. Dealuminated Y zeolite can be treated with MAO and then Cp_2ZrCl_2 to give an active supported catalyst for ethylene polymerization [400]. The most active catalyst was that supported on a zeolite with a high Si/Al ratio. Clays and solid acids are also suitable supports for a Cp_2ZrCl_2–$AlMe_3$ catalyst [401] although the same catalyst supported on phosphotungstic acid and silicomolybdic acid did not exhibit any catalytic activity [401a]. The mesoporous silicate MCM-41 can be allowed to react with MAO to form a supported activator and then contacted with *rac*-Et(Ind)$_2$ZrCl$_2$ to afford a heterogeneous catalyst. Polypropylene formed from this catalyst has a melting point well above that from the homogeneous counterpart (141 vs. 128°C) [402]. An examination of the supported catalyst by EXAFS shows that the bis(indenyl) structure remains intact and that a short Zr–C bond exists, but no chlorides [403]. Talc with a mean particle size of from 2–10 μm and allowed to react with Bu_2Mg–$AlEt_3$–butanol forms a support for a Cp_2ZrCl_2–MAO catalyst system [404]. Polysiloxanes bearing cyclopentadienyl functionalities can be deprotonated and allowed to react with $CpMCl_3$ to form polymeric procatalysts for ethylene polymerization [405]. Propylene polymerization in pentane using SBS block copolymers as a dispersing agent produces polymer particles with good morphology and low fines content [406].

The procatalyst $Cl_2Si(Ind)_2ZrCl_2$, when allowed to reacted with $MgCl_2$, also affords a supported metallocene; the silyl chlorides are presumed to bind to the Lewis-acidic $MgCl_2$ as in **88** [407].



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When activated by MAO, this catalyst was far more active than the analogous $Me_2Si(Ind)_2ZrCl_2$–$MgCl_2$ system. Likewise the polar group in $MeO_2CCH_2CpTiCl_3$ binds to $MgCl_2$ to form a solid catalyst which is activated by Al(*i*-Bu)$_3$ for propylene polymerization [408]. Sarma and Sivaram report that Cp_2TiCl_2 supported on $MgCl_2$ is a more active catalyst at 70°C than the homogeneous counterpart, affording polymer of higher molecular weight with narrow polydispersities [409].

Polymeric materials also make suitable carriers for single-site catalysts. Polyethylene itself has been employed by careful low-temperature and -pressure prepolymerization of a Cp_2ZrCl_2–Al(*i*-Bu)$_3$–$[HNMe_2Ph][B(C_6F_5)_4]$; the granular product can then be used at more demanding process conditions [410]. The reaction of maleic anhydride grafted polypropylene with MAO affords a supported activator which can be used with a wide variety of metallocene dichlorides [411]. An acrylonitrile–divinylbenzene copolymer treated with ethylenediamine has also been used successfully as a support for Cp'_2ZrCl_2–MAO catalysts [412].

The adsorption of $Et(Ind)_2ZrCl_2$ on silica was examined using modified extended Hückel methods. At 200°C, the metallocene adsorbs on the (100) plane containing geminal –OH groups preferentially to the (111) plane containing isolated hydroxyls; treatment with MAO (simulated as an AlO layer) stabilizes the adsorbed metallocene in both orientations. At 600°C, the adsorbed metallocene is stable in both planes, but aluminum inhibits coordination [413].

24. Mixed single-site and single-site-Ziegler catalysts

A perceived deficiency in polymers produced from single-site catalysts is that their narrow molecular weight distribution makes processing more difficult. In order to overcome some of these difficulties, as well as producing polymers with superior properties, mixtures of single-site catalysts are used or combinations of single-site catalysts and conventional Ziegler–Natta catalysts.

Ethylene-1-octene copolymers of varying crystallinities—produced from 'constrained-geometry' cyclopentadienyl amide titanium catalysts—have been blended to produce resins with superior softening point and Shore hardness than the individual components [414]. Thermoplastic elastomers result from the polymerization of propylene by the combined catalyst $Me_2Si(Ind)_2ZrCl_2$ (isospecific component) and $Et(Flu)_2ZrCl_2$ (aspecific component) cocatalyzed by Al(*i*-Bu)$_3$–$[Ph_3C][B(C_6F_5)_4]$; the polymer properties can be varied considerably by adjusting concentrations of the individual catalyst components [415]. Late transition metal catalysts like $(ArN{=}C(R)–C(R){=}NAr)NiX_2$ were combined with metallocene catalysts or conventional Ziegler–Natta systems to produce broad molecular weight distribution polyethylenes and polypropylenes [416].

Polyethylene from a silica-supported $Et(Ind)_2ZrCl_2$–Cp_2HfCl_2–MAO catalyst shows surprising variations in molecular weight distribution as the pressure is increased. At low pressures (5 psi) the MWD is broad and unimodal. At intermediate pressure (50–150 psi), a bimodal MWD is observed, which becomes narrow and unimodal as the ethylene pressure is increased to 200 psi. The zirconocene fraction is unaffected by the change in pressure—indicative of chain transfer to monomer—while the molecular weight of the hafnocene fraction increases, suggesting that β-hydride elimination is the predominant chain-transfer mechanism [417].

There is a sizable variety of catalyst formulations and polymerization methods in hybrid single-site-Ziegler–Natta catalysts. The non-metallocene component may be a cobalt salt [418], a chromium salt or chromocene [419], a $TiCl_4$–$VOCl_3$ mixture [420], or a Mg(Bu)(Oct)–$SnCl_4$–$TiCl_4$ mixture [421]. A magnesium siloxide, formed from dibutylmagnesium and poly(methylhydrosilane) forms the support for a Cp_2TiCl_2–$TiCl_4$–$AlEtCl_2$ catalyst [422].

The activity of one binary catalyst was improved when $(n\text{-BuCp})_2ZrCl_2$ was contacted with MAO (not $AlMe_3$ or $AlEt_3$) before addition to the $TiCl_4$–Bu_2Mg–butanol–silica mixture [423]. Adding Cp′Li (Cp = Cp, Ind) to a $TiCl_4$–$MgCl_2$ catalyst increases the activity considerably, though the catalyst behavior (hydrogen sensitivity) and polymer properties (broad MWD) are closer to that of a conventional Ziegler system than that of a metallocene catalyst [424].

While the single-site/non-single-site hybrid catalyst is usually added to the reactor as a single component, polymerization is also possible by using a conventional Ziegler–Natta catalyst in a first stage, interrupting or terminating the polymerization, and adding a metallocene catalyst (in this case, a $Zr(O\text{-}n\text{-}Pr)_4$–Indene–$AlEt_3$ catalyst) in a second polymerization stage [425].

Isotactic/syndiotactic polypropylene blends are formed from a combined conventional supported Ziegler–Natta catalyst (isotactic) and a $Me_2C(Cp)(Flu)ZrCl_2$–MAO catalyst (syndiotactic) [426]. Porous polypropylene produced from a conventional Ziegler–Natta catalyst was subsequently contacted with an $Et(H_4\text{-}Ind)_2ZrCl_2$–MAO catalyst using incipient wetness methods; the subsequent formulation was used to copolymerize ethylene and propylene, thus forming an impact copolymer [427].

25. Other process considerations

A continuous stirred-tank reactor was used to study the kinetics of ethylene polymerization using a Cp_2ZrCl_2–MAO catalyst. Increasing catalyst concentration led to a decrease in polymer molecular weight, as did increasing the temperature from 140 to 200°C. The molecular weights could be increased to a constant level by increasing the ethylene pressure or by increasing the residence time of the catalyst [428]. The gas-phase polymerization of ethylene using a silica-supported $Me_2Si(Ind)_2ZrCl_2$–MAO catalyst shows that catalyst activity increases with increasing temperature, but catalyst deactivation does as well; kinetic models indicate a first-order dependence on the rate of polymerization [429].

The presence of long-chain branching is believed to arise from reincorporation of vinyl-terminated macromers in a growing polymer chain. Modeling of a single-catalyst polymerization suggests that the MWD will broaden with increasing long-chain branching. The model suggests that narrow MWD branched polymers should have comb-like structures; these can be prepared from a two-catalyst system, one for macromers, one for the main chain [430]. Analytical models for chemical composition distribution predict narrowing CD with increasing long-chain branching populations [431].

A steady-state kinetic model for polymerization by a homogeneous catalyst was developed and applied to the data reported for polymerization by $(Me_2NCH_2CH_2Cp)TiCl_3$–MAO and other metallocene catalysts [432]. A transient-state kinetic model was derived as well to account for, among other things, inequalities between the rate of monomer consumption and the rate of polymer growth [433].

A technique has been developed by researchers at Union Carbide to polymerize olefins in a fluidized bed gas-phase reactor using *unsupported* single-site catalysts. A spray gun is used to inject a mixture of (Ind)Zr(O_2C-*t*-Bu)$_3$ and MAO in an ethane-isobutane solution as an aerosol into the gas-phase reactor above the distributor plate perpendicular to the direction of monomer flow [434].The technique was also used to polymerize propylene to isotactic PP using a *rac*-Me_2Si(2-Me-4-Ph–Ind)$_2ZrCl_2$–MAO catalyst [435]. Use of a 'supercondensing' co-fluidizing agent such as isopentane improves the space time yield of the process [436].

Polyethylene with broad molecular weight distribution is formed from a single metallocene catalyst by carrying out the polymerization in a first stage, then transferring the catalyst to a second stage polymerization with different reactor conditions; a polymer with a melt flow ratio (MFR) of 20 is produced from the first stage, but the final blend has an MFR of 56 [437]. Carrying out propylene polymerizations under supercritical conditions using a silica-supported Et(Ind)$_2ZrCl_2$ or Me_2Si(Ind)$_2ZrCl_2$ catalyst with MAO results in roughly a doubling of catalyst activity [438].

By operating a gas-phase polymerization process at an ethylene partial pressure of 200 psi or less, polyethylenes produced from supported metallocene catalysts have improved flow and processibility characteristics [439]. The molecular weight of polymers produced from supported metallocene catalysts is improved when generated hydrogen is removed from the gas stream. This is done by taking a slip stream of recycle gas over a palladium catalyst [440]. Catalyst performance in an isobutane slurry process is improved by contacting the diluent with Raney copper to remove methanethiol [441].

MAO solutions can form gels over time, which can cause fouling in supported catalysts. Adding metallocene complexes to the MAO appears to stabilize the solution and retard gel formation. Even after a month, these metallocene–MAO solutions can be supported on silica and the supported catalyst used without fouling [442]. Stable, non-pyrophoric metallocene–MAO mixtures are formed by adding a toluene solution of the catalyst to paraffin oil or petroleum jelly and stripping of the volatile component; good aging properties are observed [443]. Bulky, non-polymerizable olefins such as vinylcyclohexane or vinyltrimethylsilane appear to stabilize metallocene–MAO mixtures, improving catalyst performance [444].

Polymerizations using catalysts activated by boron-based cocatalysts are particularly prone to deactivation by adventitious impurities. A $Me_2Si(C_5Me_4)$(N-*t*-

Bu)Ti(1,3-pentadiene)-B$(C_6F_5)_3$ catalyst maintains high activity when a dialkylaluminum alkoxide like diisobutylaluminum(2,6-di-*t*-butyl-4-methylphenoxide) is used as a scavenging agent [445]. The high temperature and pressure performance of hafnium metallocenes activated by trityl or dimethylanilinium salts of $[B(C_6F_5)_4]^-$ is enhanced when long-chain aluminum alkyls such as tri(*n*-octyl)aluminum are added to the system to remove oxygen and water [446].

Bulk monomer or gas-phase polymerizations and copolymerizations of α-olefins can be carried out without fouling of walls or agitators by blending the catalyst with a commercially available antistatic agent or by injecting a solution of the antistat into the process [447]. Stabilized polymers are produced by prepolymerizing a metallocene–MAO catalyst, letting down the pressure, adding a stabilizer like tris(2,4-di-*t*-butylphenyl)phosphite, and repressurizing the system to continue the polymerization [448].

The activity of a homogeneous metallocene catalyst is enhanced by adjusting the dielectric of the solution. This is done by adding a weakly-coordinating donor like trifluoromethylphenyl ether or 2,2,5,5-tetramethyltetrahydrofuran [449]. The initial spike in catalyst activity often observed in metallocene polymerization catalysts can be moderated by adding a retardant like 9-BBN or DIBAL-H [450].

Conventional Ziegler–Natta catalysts and metallocene catalysts frequently respond quite differently to temperature, pressure, and hydrogen concentration in continuous processes. The transition should be smooth and not require shutting down the reactor. Deactivation of a chromium catalyst with isopropanol allows introduction of metallocene catalyst, and the metallocene catalyst can be deactivated with CO_2 in order to transition to a Ziegler system [451]. Polymer product can be deashed effectively by treatment with water- or methanol-laden nitrogen stream [452].

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