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REVIEW

The Design of Group 4 Cyclopentadienyl, Olefin-Polymerisation Catalysts

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Abstract

This review focuses on Group 4 metallocenes and their use in the polymerisation of α-olefins. A brief overview of their history as well as theories concerning the mechanistic details of the polymerisation reaction precedes a discussion on the design of these polymerisation catalysts. This latter section will cover what effect metal, ligand and bridge choice has on polymerisation activity and the physical properties of the polymer produced. A major drawback to the use of these catalysts in industrial processes is related to the cost of their synthesis, the major problem here being the formation of an unwanted diastereomer during the synthetic process. The techniques employed to overcome these problems are therefore also reviewed. Lastly, the large volume of literature dealing with these catalysts makes it difficult to compare the polymerisation data of different catalysts and laboratories. The review therefore contains tables that attempt to collect the details of the most important polymerisation studies in a comparable and easy to reference manner.

Keywords Homogeneous catalysis; Titanium; Zirconium, Hafnium; Indenyl; Cyclopentadienyl; Fluorenyl.

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1. Introduction and Historical Perspective

Catalysis is the key to efficient chemical processing and most industrial reactions are therefore catalytic. These processes include the manufacturing of food, fuels, polymers and pharmaceuticals to name but just a few. Transition metals are invariably employed in the most successful catalysts, with their d-orbitals bonding to chemical substrates such as H, CO and olefins. However, the metal cannot operate in isolation as a catalyst and is therefore always surrounded by groups or atoms (ligands). It is the ligands bonded to a metal atom(s) that strongly influence the course of a reaction. A systematic modification of the ligand can therefore bring about a specific change in both the rate of a reaction and the final product(s) formed. This is done through either ligand steric or electronic effects, but more commonly, a combination of both. Large ligands will, for example, prevent substrates beyond a certain size from approaching the metal. Also, excessive stability of the bond between the metal and substrate must be avoided as this slows down or prohibits catalysis.

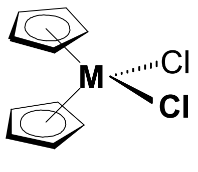
Metallocenes catalysts that are capable of polymerising α-olefins into useful materials have proven to be very successful. The first of these catalysts, bis(cyclopentadienyl)titanium dichloride (**1**) was synthesised almost 50 years ago by Wilkinson and Birmingham.[1] Its ability to polymerise ethene to polyethene, after activation by an aluminium co-catalyst, was discovered shortly thereafter by Natta[2] as well as Breslow and Newburg.[3,4] This did not however result in any commercial applications of this complex due to the low polymerisation activity of this catalyst. Instead, in the 1960's and 1970's metallocene α-olefin polymerising catalysts were studied to obtain mechanistic information about the commercially successful heterogeneous catalysts.

Reichert and Meyer found that by adding small amounts of water to the **1**/C_2H_5AlCl system, much higher polymerisation activities could be achieved.[5] Long and Breslow published similar findings two years later in 1975. They found that adding water, *ca*. 0.2-0.5 mole per mole aluminium, resulted in extremely active catalysts being formed.[6] It was however Sinn and Kaminsky who discovered that a very active co-catalyst could be synthesised by the controlled addition of water to trimethylaluminium, thereby generating an alkyl-aluminoxane.[7-9] These metallocene-aluminoxane systems were found to be 10 000 times more active than the traditional aluminium alkyl (R_nAlCl_{3-n}) co-catalysed analogues. Not only ethene, but propene could also now be polymerised. Further, previously catalytically inactive metallocenes such as Cp_2ZrCl_2 (**2**) were also found to display catalytic activity.

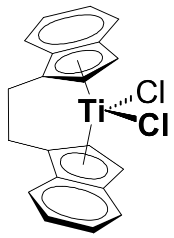
Another defining moment in this area of research was the synthesis of a bridged metallocene, $Et(Ind)_2TiCl_2$ (**3**), by Brintzinger in 1982.[10] Ewen[11] was later able to use this compound to polymerise propene to partially isotactic polypropylene and shortly thereafter Kaminsky and Brintzinger were able to obtain highly isotactic polypropylene using the analogous tetrahydroindenyl zirconocene, $Et(IndH_4)ZrCl_2$ (**4**).[12]

It was these latter two discoveries, *viz.* the discovery of aluminoxane co-catalysts and stereoselective catalysts, that has driven research in the area of Single Centre Catalysts (SCC's) from laboratory curiosity to commercially viable systems. In the past 20 years there has hence been a fervent scramble amongst academic and industrial research groups to synthesise better catalysts. In this review, these catalysts are distinguished from the classical heterogeneous Ziegler-Natta (Z-N) catalysts, which have been extensively and very profitably used in industry for the past four decades. SCC's differ in that they have very well defined molecular structures. The active sites, which make up the active centre of a catalyst, co-ordinate the incoming olefin monomers and insert them into the growing polymer chain. The similarity of all of the active centres in a SCC results in all the polymer chains produced being similar to each another. The polymers formed from Z-N catalysts in turn have a broader molecular weight distribution as a result of differences in their active centre morphologies, an artefact introduced through their synthesis.

The large number of review articles that have appeared in the literature recently attest to the importance of SCC-research.[13-42] An overview of these articles, listed in Table 4 (see Appendix), reveal that SCC's no longer solely encompasses Group 4 metallocenes with cyclopentadienyl-type ligands such as **1**-**4**. Amide and alkoxide ligands bound not only to Group 4 metals, but also the later transition metals such as iron, cobalt, nickel and palladium, have been found to form very active and unique catalysts. Two recent reviews have very adequately described recent advances made in this area.[29,30] The work presented in this review concerns the former cyclopentadienyl-type metallocenes of the general formula Cp_2ZrCl_2 (Cp = Cp, Ind or Flu). The emphasis will be on the metallocene ligand modifications and the influence that this has had on their polymerisation behaviour as well as the characteristics of the polymer formed.



M=Ti **1**
=Zr **2**



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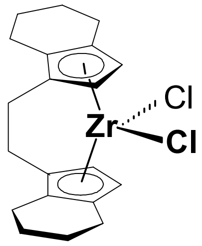

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2. The Nature of Metallocene Catalysts

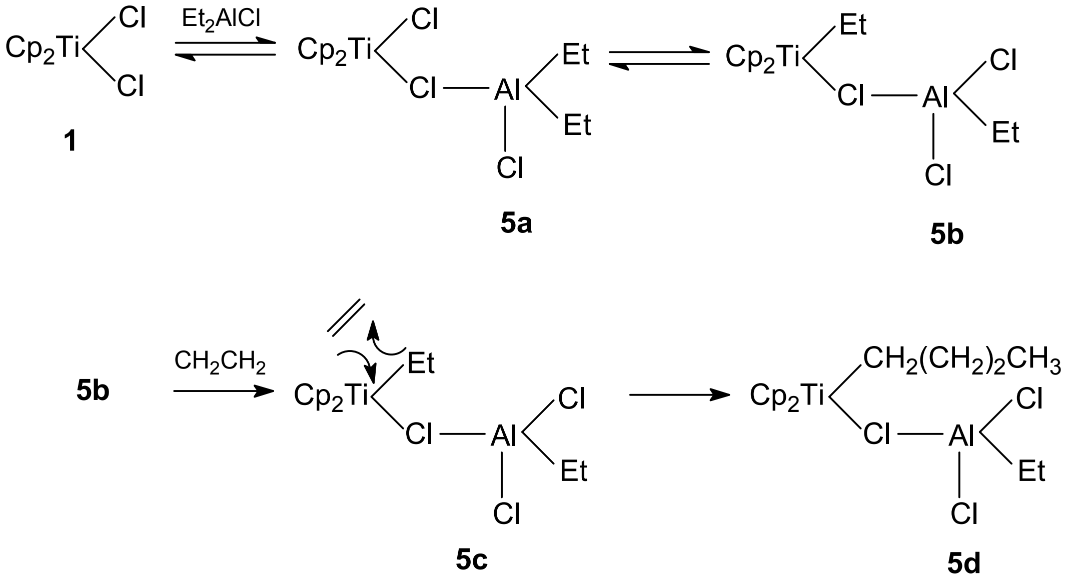
Before we commence the discussion of how metallocene ligand design has evolved, it is perhaps appropriate to give a description of the nature of the active polymerisation species. Current theories on how successive monomer insertions occur as well as the termination of the growing polymer chain will also be briefly discussed.

2.1. The Active Polymerisation Species

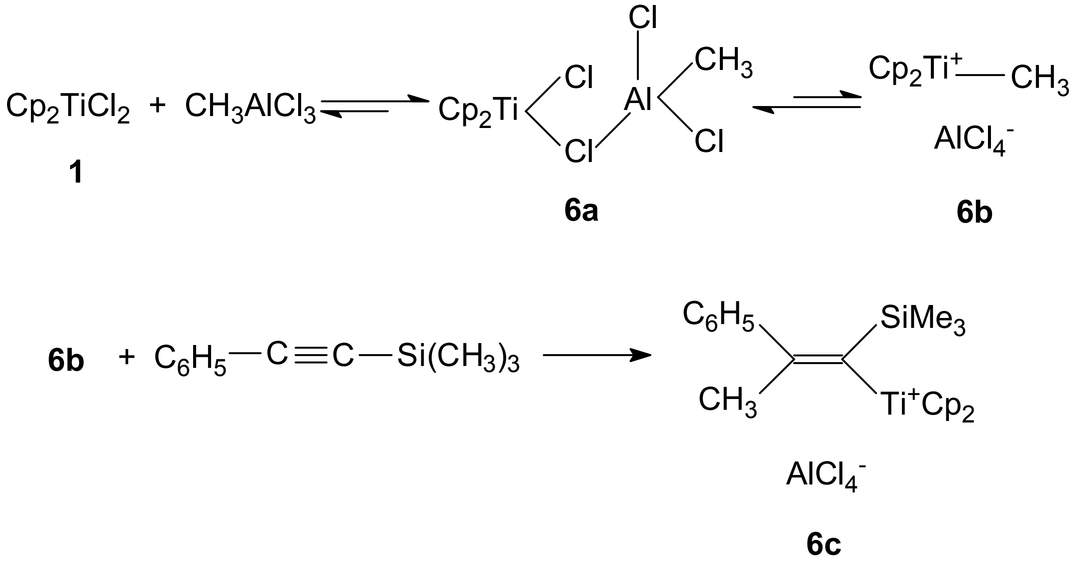
It is accepted that the active polymerisation species in metallocene type catalysts is a cationic, 14-electron metal containing species. This was first suggested by Shilov, Shilova and Dyachkovskii[43,44] in the 1960's, but it was almost two decades later before convincing evidence supporting this theory was published. Prior to this many research groups advocated a bimetallic species formed from the reaction of, for example, **1** with an aluminium alkyl, R_nAlCl_{3-n}.

Initial UV-spectroscopic work by Breslow, Newburg and Long to try and elucidate the nature of the active polymerisation species, suggested that the reaction of **1** with Et_2AlCl gave the complex $Cp_2Ti(Cl)(Et)\cdot EtAlCl_2$ (**5b**, Scheme 1).[3,45] This complex, or some species in equilibrium with it was suggested to be the active catalyst. Similar bridged complexes were suggested by Henrici-Olivé and Olivé[46,47] to be directly involved in the insertion of ethene.

In 1985 Eisch and co-workers published a paper that made it possible to dismiss the idea of a bridged Cp_2TiCl_2–R_nAlCl_{3-n}, two-component catalyst.[48] By reacting **1** and CH_3AlCl_2 with a highly substituted surrogate for ethene, namely, trimethyl(phenylethynyl)silane, they were able to trap the insertion product (**6c**, Scheme 2), thereby showing that **6b** was the active species and not **6a**. Further, the possibility that **6a** was the active catalyst was dismissed by the kinetic work of Fink, who found that the rate of ethene polymerisation could only be explained if *two* equilibria were involved in creating the active species.[49]

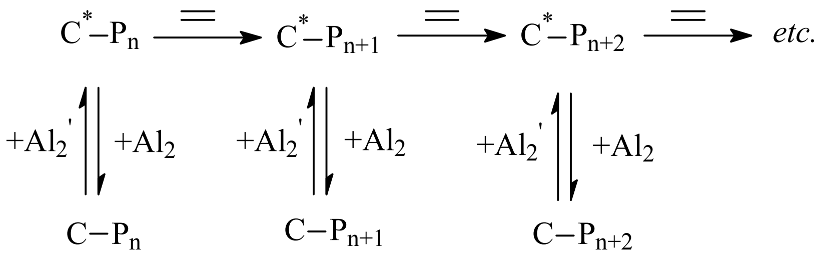


Scheme 1 The bimetallic species, **5b**, was originally thought to be responsible for ethene insertion and polymerisation.



Scheme 2 Reaction devised by Eisch and co-workers to disprove that the bimetallic system **6a** is responsible for ethene insertion. Instead, a cationic species **6b** was shown to be the active polymerisation catalyst.

The kinetic studies by Fink[49-51] showed that when an aluminium alkyl reacted with Cp_2TiCl_2, an active species C^* is formed (Scheme 3). This species not only inserted successive ethene molecules, but could also be reversibly converted into a dormant state, $C–P_n$. This dormant species was spectroscopically detectable.



Scheme 3 Reaction scheme, as proposed by Fink, illustrating the insertion of ethene into an active polymerisation species ($C–P^*_n$) as well as the transition of this species to a dormant state ($C–P_n$) facilitated by an alkylaluminium compound. Al_2' = unknown, Al_2 = $(AlEtCl_2)_2$, P_n = polymer chain.

It was Jordan, Bochmann and co-workers who however provided further proof that cationic species are directly involved in polymerisation reactions.[17,52] They were able to show that cationic 14-electron metallocenes, *free* of aluminium alkyl co-catalyst, could be used as olefin polymerisation catalysts. Crucial to the activity of these cationic catalysts is the need for the presence of a very weakly co-ordinating counterion. If this counterion was bound too strongly to the active site, the monomer molecule was not able to displace the counterion and hence polymerisation was not possible. Compounds with perfluoronated phenyl rings, such as $B(C_6F_5)_4^-$, first employed by Hlatky and Turner, have proved to be very successful weakly co-ordinating counterions in this respect.[53]

Work involving neutral Group 3 and lanthanide metallocenes, Cp_2MR, have also provided evidence for a 14-electron active species. These compounds are isoelectronic with the cationic analogues mentioned above and have been shown to exhibit polymerisation activity.[54-58]

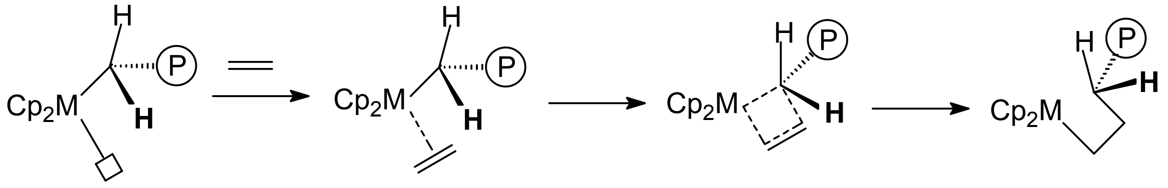
2.2. Polymerisation Mechanism

The reaction path followed by Z-N and SCC's when polymerising α-olefins has elicited much interest and speculation from researchers over the years. The unravelling of the mechanistic details provides vital evidence that can be used in the synthesis of better commercial catalysts. For the purpose of this discussion, the reaction mechanism may be broken down into two parts, *viz.* monomer insertions resulting in polymer growth and chain transfer processes that determine the chain length of the polymer.

2.2.1. Monomer Insertion and Chain Growth

Monomer insertion and polymer growth are believed to occur *via* a mechanism similar to that proposed by Cossee and Arlman (Scheme 4).[59-61] According to this mechanism, the monomer pre-coordinates to the active complex leading to the formation of a π-complex. This leads to an *alkyl migration* to the bound monomer resulting in the formation of a new carbon-carbon bond. At no point is there an interaction of the C–H bonds of the alkyl chain with the metal. Rooney and Green proposed a modified version of this mechanism in which the growing polymer chain undergoes a 1,2-hydrogen shift to give a metallocarbene, which precedes monomer insertion (Scheme 5).[62,63]

There are many examples in organometallic chemistry where agostic[1] interactions have been shown to play a role.[65] The presence of an agostic bond arises from the electron deficiency at a metal coupled to its co-ordinative unsaturation and/or lack of steric protection.



Scheme 4 Carbon-carbon bond formation as described in the Cossee-Arlman reaction mechanism.

These two mechanistic proposals can be thought of as extreme representations of the chain growth processes. Numerous theoretical and experimental studies, discussed below, instead point to an intermediate pathway, which lies somewhere between the Cossee-Arlman and Green-Rooney mechanisms. Two improved mechanisms have therefore been proposed.

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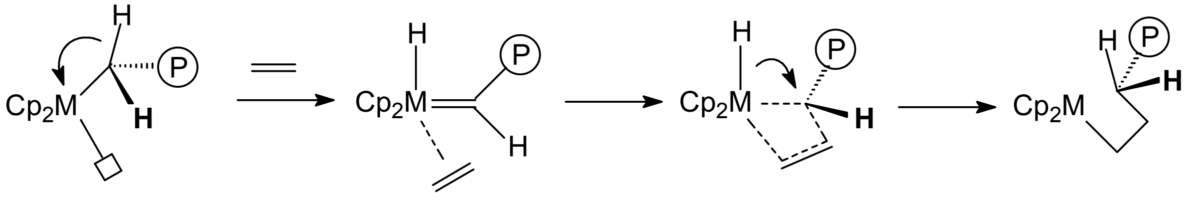
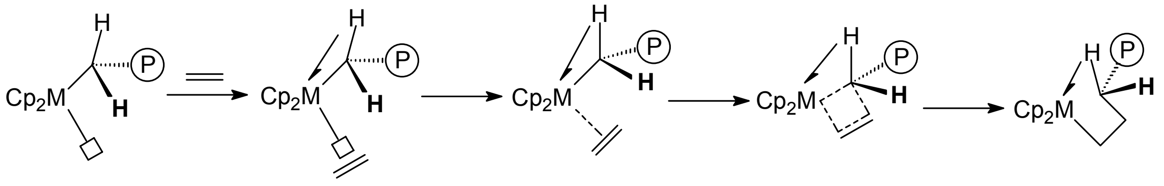
[1] Term coined by M. Brookhart and M.L.H. Green. It is derived from the Greek word ¯(@FJ`H (taken in turn from Homer's *The Iliad*), meaning to clasp or hold onto oneself.[64,65]



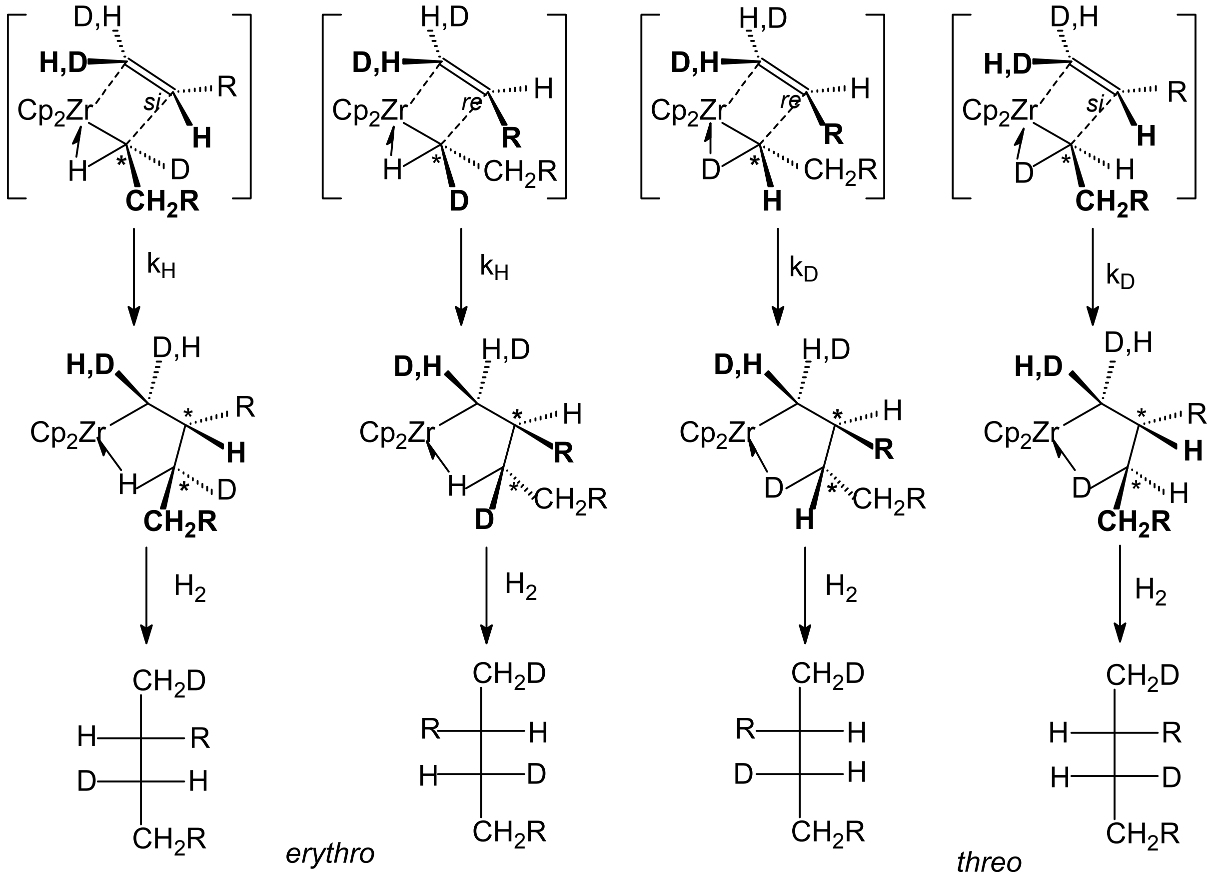
Scheme 5 In the Green-Rooney mechanism a 1,2-hydrogen shift, to form a metallocarbene, precedes monomer insertion.

The first, the modified Green-Rooney mechanism put forward by Brookhart and Green,[64,65] stresses the importance of agostic interactions *throughout* the insertion process (Scheme 6). However, in a recent review article on agostic interactions in metallocene polymerisation catalysts, Grubbs and Coates[66] advocate a much more transitory role for the α-hydrogen. By drawing on a body of experimental research involving kinetic isotope effects, they argue that the α-hydrogen atom *only* interacts with the metal during the transition state in C–C bond formation (*i.e.* second last step in Scheme 6). It should be borne in mind that there are different mechanisms associated with different catalysts, with ligand structural features playing an important role in dictating the importance of agostic interactions during the polymerisation reaction. This point will be further considered in Section 3, which entails a discussion of the structural features in metallocene catalysts.



Scheme 6 In the Brookhart-Green mechanism, the α-H of the polymer chain bonds agostically to the metal during the insertion. What has not been shown in this scheme is how the γ-agostic interaction in the final step reverts to a more favoured α-agostic one.

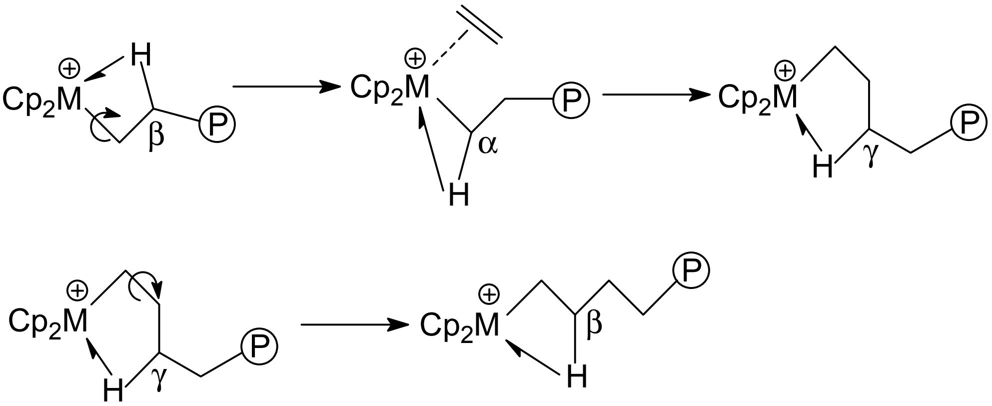
The use of kinetic isotope effects to probe the polymerisation mechanism, first proposed by Grubbs,[67] has been most elegantly put to use by Brintzinger and his co-workers.[68-70] By employing the knowledge that a Zr–H interaction is preferred over that of a Zr–D interaction, it was shown that α-agostic interactions exist when (*E*)- and (*Z*)-1-D-1-hexene as well as (*E*)- and (*Z*)-propene-1-D were polymerised. In the former case, a higher ratio (1.3:1) of the *erythro* to *threo* product was explained by the role of a favoured α-H agostic interaction with the metal during the rate-determining insertion step (Scheme 7). Piers and Bercaw observed similar isotope effects using scandium catalysts in the hydrocyclisation of *trans*, *trans*-1,6-d_2-1,5-hexadiene.[71]



Scheme 7 By exploiting the fact that the agostic interaction of H is preferred to that of D, Brinztinger was able to prove the existence of agostic interactions. In the hydrodimerisation of (E)- and (Z)-1-[D]-1-hexene, the erythro diastereomers were formed in a higher ratio than that of the threo (1.3:1).

A considerable body of work from theoretical studies has been gathered on the metallocene olefin polymerisation mechanism. These studies not only try to map out the details of the olefin insertion, but also attempt to explain the tacticity of the polymer produced by a particular catalyst in the polymerisation of a prochiral monomer such as propene. This work encompasses the use of quantum mechanics (*ab initio*, density functional theory and semi-emperical methods), molecular mechanics (molecular mechanics and molecular dynamic approaches) or a combination of both. Important issues relating to this area of research has been covered in two recent reviews.[37,38]

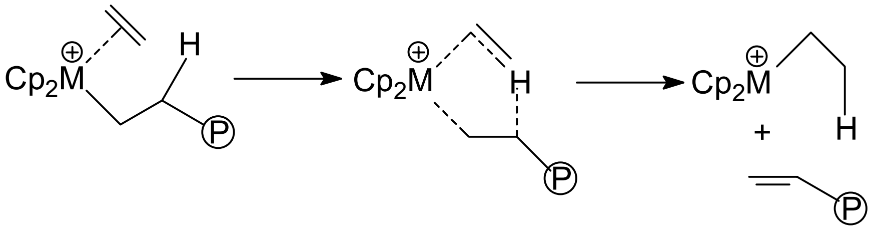
The results provided by these theoretical studies tend to depend, however, on the weight given to agostic interactions, but most agree on the following mechanistic details. The resting state of the active polymerisation catalyst is a species that contains a β-agostic interaction. Front-side insertion of the monomer is then most likely, but before this can occur, rotation of the polymer chain about the M–C_α bond must occur. This results in an α-agostic stabilised transition-state. This rotation is thermodynamically favoured over β-elimination. Insertion can then occur to give a γ-agostic product which then either reverts to the more stable β-agostic resting state or continues with the insertion process (Scheme 8).[72-80]



Scheme 8 Before ethene inserts into a polymer chain, a rotation around the M-C_α bond occurs to give an α-agostic intermediate. The product, which is a γ-agostic intermediate revert to the more stable β-agostic species.

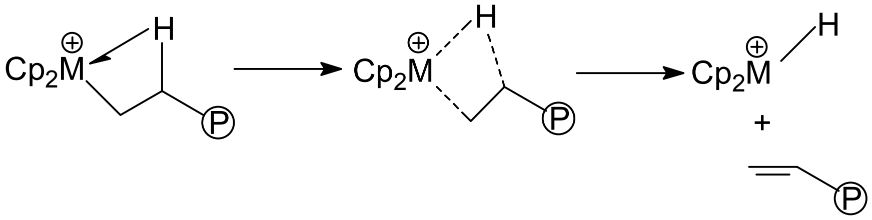
2.2.2. Chain Transfer Mechanisms

Termination of the growing polymer chain can occur through several pathways. The most common chain transfer processes that can occur are: (i) β-H transfer to either the metal or co-ordinated monomer, (ii) β-alkyl transfer to the metal or (iii) chain transfer to aluminium. Chain termination may also be effected by the addition of H_2 to the polymerisation reactor and this procedure is usually employed in industry to lower the molecular weight of the polymer produced. By studying the chain-ends of the polymers we can identify the termination pathway(s) followed by a particular catalyst.



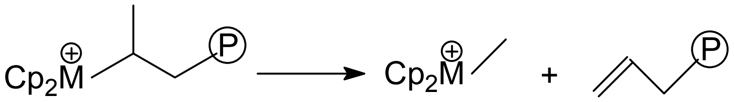
Scheme 9 Chain termination by transfer to co-ordinated monomer.

The first of these processes, β-H transfer to a co-ordinated monomer (Scheme 9) or metal (Scheme 10) produces vinyl-terminated polymers and alkane terminated chains when ethene is polymerised. When propene is the monomer, these termination reactions result in vinylidene and *n*-propyl end groups. Theoretical studies have, however, indicated that transfer to the metal is an endothermic process with transfer to the monomer being thermodynamically more likely.[74-77,79,80]



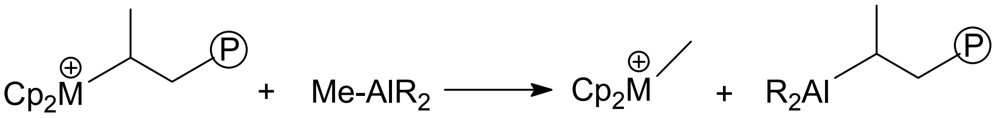
Scheme 10 Termination by chain transfer to the metal.

The second chain transfer mechanism is a β-Me transfer to the metal (Scheme 11). This usually occurs in the polymerisation of propene and is especially prevalent when the ligands attached to the metal are highly substituted.[81] Allyl terminal groups result from this process.



Scheme 11 β-Me transfer to the metal resulting in the formation of an allyl end-group.

Chain transfer of the polymer chain from the catalyst to an aluminium centre results in saturated polymer chain ends once the polymerisation reaction is terminated (Scheme 12). When propene is polymerised, this results in *iso*-propyl chain ends being observed in the NMR-spectra of the polymer.



Scheme 12 Chain transfer of the polymer to an aluminium centre.

3. The Design of Metallocene, Olefin Polymerisation Catalysts

The physical properties of the polymers produced by metallocene catalysts are dependent on a number of factors. These include the reaction conditions employed during the polymerisation (*e.g.* temperature and pressure), the monomer-type(s) fed into the reactor and most importantly, the catalyst used to stitch the monomers together. It is the design of the catalyst that dictates not only the amount of polymer formed, but also its properties.

One of the most actively researched catalyst types has been the Group 4 metallocenes. In this section we discuss what has been learnt about ligand design and the rules applied to achieve a desired result.

3.1. The Effect of Metal on Polymerisation Results

The choice of the Group 4 metal used in these metallocene catalysts has a profound influence on the polymerisation reaction. For bis-cyclopentadienyl metallocenes, the activity order is usually Zr > Ti > Hf whereas the molecular weight of the polymers produced decrease in the order Hf > Zr > Ti.[82-89] This ordering may be explained by steric and electronic factors. The Ti atom has a smaller radius than Zr and Hf, which are similar in size. This results in more congested transition states during polymerisation reactions where agostic interactions and chain rotations have to occur. Therefore, any extra steric congestion introduced by the ligands bonded to the metal result in a marked drop in polymerisation activity.[90] The polymerisation activities of the Constrained Geometry Catalysts (CGC's)(Figure 1) bear this out. Here the Ti-catalysts have a higher activity than Zr followed by Hf.[91] Theoretical studies confirm these findings where it has been shown that the insertion barriers for Ti-CGC's are lower than that of Zr and Hf CGC's,[92] whereas for the bis-cyclopentadienyl catalysts, the opposite result holds true.[75] The increased polymer molecular weights of the Hf catalysts are due to the stronger bonds they form to the polymer chain and the co-ordinated monomer. This phenomenon results in fewer terminations by β-H transfer compared to their Zr analogues where faster monomer insertions take place, and hence higher activity occurs.

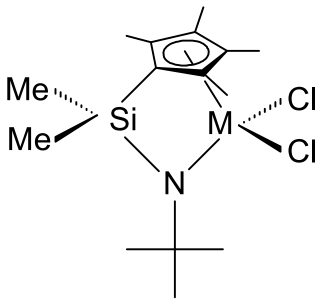
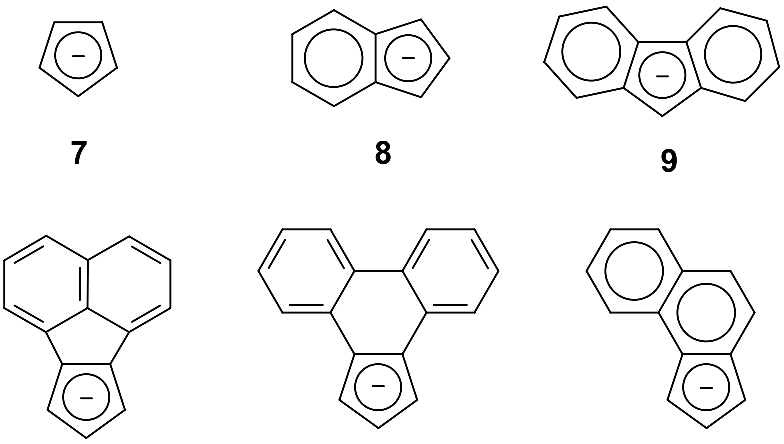


Figure 1 A constrained geometry catalyst.

3.2. The Cyclopentadienyl Ligand

The cyclopentadienyl family of ligands has up until recently been the choice of ligand used in organometallic polymerisation catalysts. Of these, the cyclopentadienyl (Cp, **7**), indenyl (Ind, **8**) and fluorenyl (Flu, **9**) structures have been most often used. Others that have for example been employed include the cyclopenta[*a*]acenaphthadienyl (**10**),[93] cyclopenta[*l*]phenanthryl (**11**)[94,95] and benz[*e*]indenyl (**12**)[96-98] ligand systems (Figure 2). Each of these has a different steric and electronic impact on the polymerisation ability of a catalyst.



7 **8** **9**

10 **11** **12**

Figure 2 Examples of the cyclopentadienyl family of ligands.

The steric bulk imposed on the parent ligand decreases in the order **9** > **8** > **7** (Steric effects are discussed more fully in Section 5). What is less obvious though is the electronic impact these ligands have on the attached metal. Various studies have been undertaken to probe the electronic properties of these ligands and the effect they have on the electron density at the metal. One of the most effective methods of measuring this electron density is the use of gas-phase Electron-Transfer Equilibrium (ETE) techniques. In these techniques free energies for the oxidation of metal complexes are determined by Fourier transform mass spectrometry. The cation generated may then be reacted with a small molecule such as hydrogen and the rate of this reaction determined, with more electrophilic cations reacting faster with hydrogen. This type of study has been performed on a set of ruthenocene[99] and Group 4 metallocene[100,101] compounds. What they show is that **9** is more electron donating than **8** followed by **7**. The same result has been confirmed by X-ray Photoelectron Spectroscopy (XPS) studies.[102] This ligand-series is, however, affected by ligand substituent(s). For example, the latter XPS study indicated that the pentamethylcyclopentadienyl (Cp^*) is able to donate more electron density than the unsubstituted indenyl ligand. Another effect of the increased electron density on the indenyl and fluorenyl ligands is that they are more prone to “ring-slippage”. This results not only in decreased electron donation to the metal centre, but also in a change in the geometry of the catalyst and hence its reactivity.[23,103,104]

3.3. Metallocene Symmetry and Polymer Tacticity

Monomers such as propene are *prochiral* and the face or *topos* presented to the metal determines the stereoregularity of the polymer formed. The stereoregularity refers to the position of the monomer substituent units with respect to each other, on the polymer chain. There exist a number of different stereoregularities generated by the propene polymerisation reaction and these are depicted in Figure 3. If the methyl groups are randomly orientated, orientated all to one side or alternating with respect to the polymer backbone, the polymer is defined as being *atactic*, *isotactic* or *syndiotactic* respectively.[2] Apart from these three main structures it is also possible to polymerise propene in a stereo-block fashion where blocks of the monomer units are

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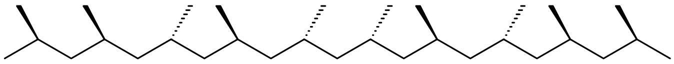
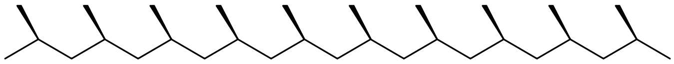
[2] The suffix *-tactic* is derived from the Greek word *tacticos*, meaning arrangement. The term was proposed by Guillo Natta’s wife.

orientated in the same way on the polymer chain. Lastly, when polymers are formed in which every second monomer unit is inserted in a random fashion with respect to the rest of the polymer chain's units, then the polymer is referred to as *hemiisotactic*.

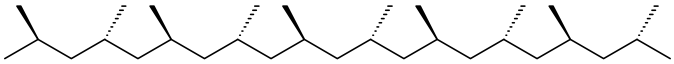
These polymer types are used to reference polymers produced by different catalyst systems. For example, the first metallocene employed to produce isotactic polymer by catalytic-site control, *rac*-ethylene-bis(indenyl)zirconium dichloride,[11] only produced a polymer that was 63% isotactic. The rest of the monomer units in the chains were inserted in an atactic fashion. Also, co-polymerisation of two monomers can produce endless varieties of structures depending on the catalyst's ability to insert the respective monomers.



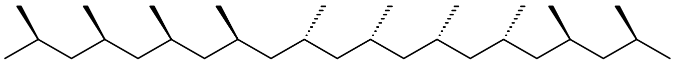
atactic



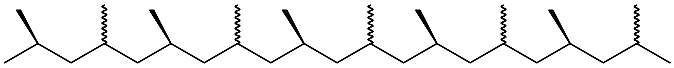
isotactic



syndiotactic



stereo-block



hemiisotactic

Figure 3 The substituent on the monomer units in the polymer chain can be positioned in different orientations to each other giving rise to different stereostructures.

One of the driving forces behind innovation in the design of metallocene catalysts has been the desire to control this stereostructure in the polymer formed. This area has recently been thoroughly reviewed by Resconi and co-workers.[33] The control of polymer stereostructure is important as each of the polymers represented in Figure 3 has vastly different physical properties suitable for different applications. For example syndiotactic polypropylene is more flexible and clearer than the isotactic polymer and is often used in the medical industry *e.g.* in blood bags.

The most effective technique used to determine the microstructure of a polymer sample is ^{13}C NMR spectroscopy. Although information can be gleaned from the methine and methylene regions, the methyl region is the most useful in this regard. For polypropylene, the chemical shift of each CH_3 is determined by the configuration of the two neighbouring CH_3 groups on each side of it and the overall effect gives rise to a signal due to a particular pentad. There are ten possible pentad signals and they can be illustrated by the Fischer projections shown in Figure 4. These fall into three groups, *viz.* *mm*-centred (*mmmm*, *mmmr*, *rmmr*), *mr*-centred (*mmrr*, *mmrm*, *rmrr*, *rmrm*) and *rr*-centred (*rrrr*, *rrrm*, *mrrm*) signals.[105] Only nine on these signals are observed as *mmrm* and *rmrr* pentads have the same chemical shift. Thus, a perfectly isotactic or syndiotactic polymer will only have one signal due to either the *mmmm* and *rrrr* pentads respectively.

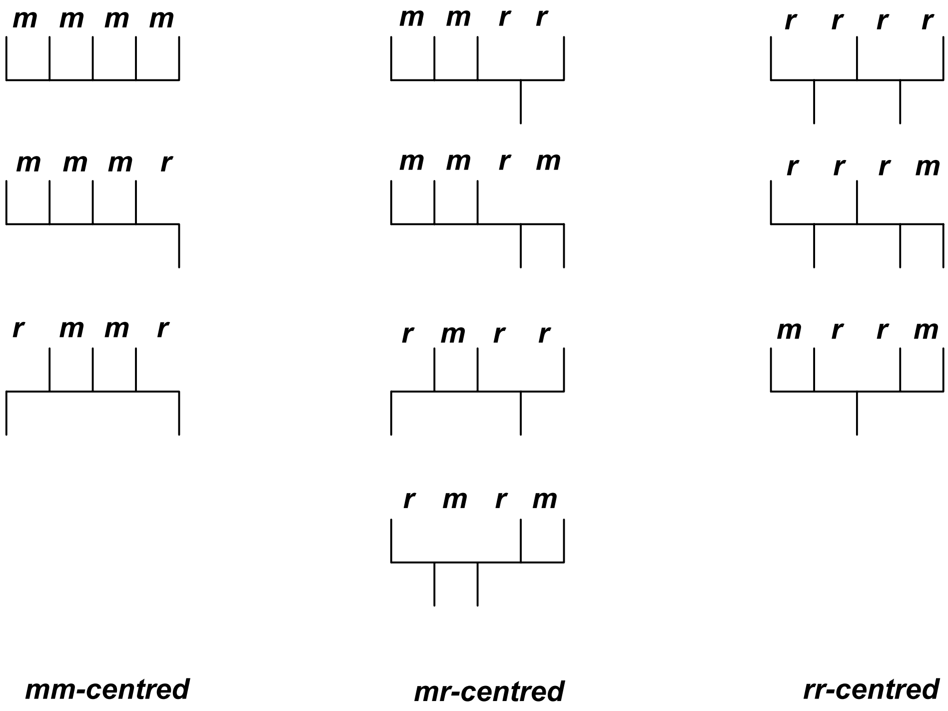


Figure 4 The ten possible arrangements of five CH_3 groups (pentads) on a polypropylene backbone.

Polymer tacticity can arise through two mechanisms, *viz.* chain end control and catalytic-site control (also known as enantiomorphic-site control). In the former, the asymmetric configuration of the last inserted monomer unit in the chain dictates the tacticity of the rest of the polymer chain whereas in the latter, this control is exercised through the active polymerisation site (Figure 5). Therefore, if there is an incorrectly inserted unit in a catalytic-site controlled catalyst, this will be corrected when the next monomer is inserted. By studying the ^{13}C NMR spectra of the polymer produced by a particular catalyst, the tacticity control mechanism exercised may be determined. Catalytic-site control gives rise to errors associated with *mmrr* and *mrrm* pentads, whereas *mmrm* pentads are observed in chain-end controlled polymers.

Ewen has recently published two brief reviews[19,106] explaining the rules behind metallocene design and polymer tacticity. The 1995 review by Brintzinger, Fischer, Mülhaupt, Reiger and Waymouth also devoted a section to this topic.[15] What was proposed is that the chirality of the catalyst dictates the type of polymer produced. These rules are generally obeyed as follows: catalysts with C_{2v} and C_1 symmetry produce atactic polymer whereas catalysts with C_2 and C_S symmetry form isotactic and syndiotactic polymers respectively. Examples of these metallocenes are presented in Figure 6. This is a general rule and exceptions, especially for C_1-symmteric catalysts, have been found. This will be more fully explained in the next section.

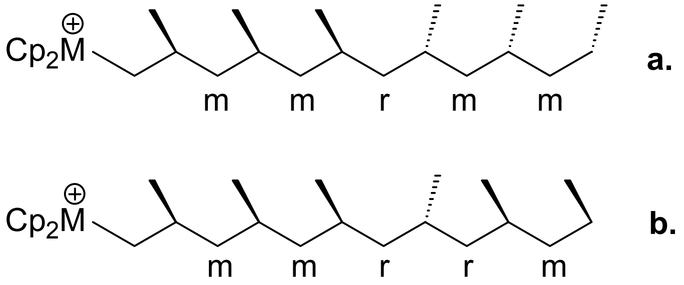
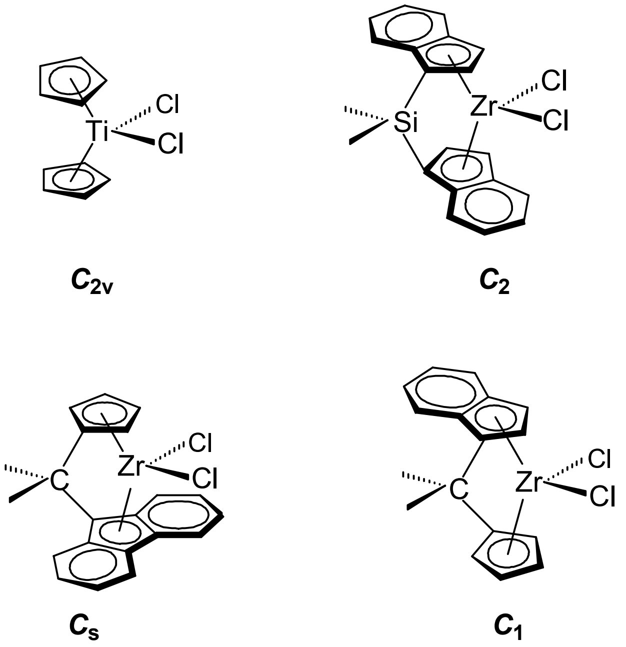


Figure 5 The last inserted unit in a chain end controlled catalysts (**a**) defines the orientation of the next inserted unit whereas for a catalytic-site controlled catalyst (**b**), any errors are corrected by the chirality of the catalyst.

Theoretical modelling studies and stereochemical analyses of polymers by ^{13}C NMR spectroscopy have proved to be potent tools in elucidating how metallocene catalysts operate. The latter, for example, not only provides information on polymer stereoregularity, but also about stereoerrors caused by misinsertions. Also, analysis of the end-groups on the polymer chain can determine which chain transfer processes have occurred.

The molecular mechanics work by Corradini and Guerra has shown the importance of the growing polymer chain and non-bonded interactions on the enantioselectivity of the catalyst.[107-113] In the approach used by these authors the area surrounding the catalyst metal centre is divided into four quadrants. As expected, the steric bulk of the polymer chain is forced into a chiral orientation, in the least congested quadrant around the metallocene due to its interactions with the π-ligands (Figure 7). This quadrant will be Q_1 and Q_3 for catalysts with C_2-symmetry and quadrants Q_2 and Q_3 in the C_S-symmetric metallocenes. Non-bonded interactions with the polymer chain then force the monomer (*e.g.* propene) to adopt an orientation with its methyl-group *trans* to the polymer chain. For C_2-catalysts the orientation of the monomer will alternate between successive insertions whereas for C_S-symmetric catalysts, the propene monomer will always have its methyl-group situated in the most congested quadrants.

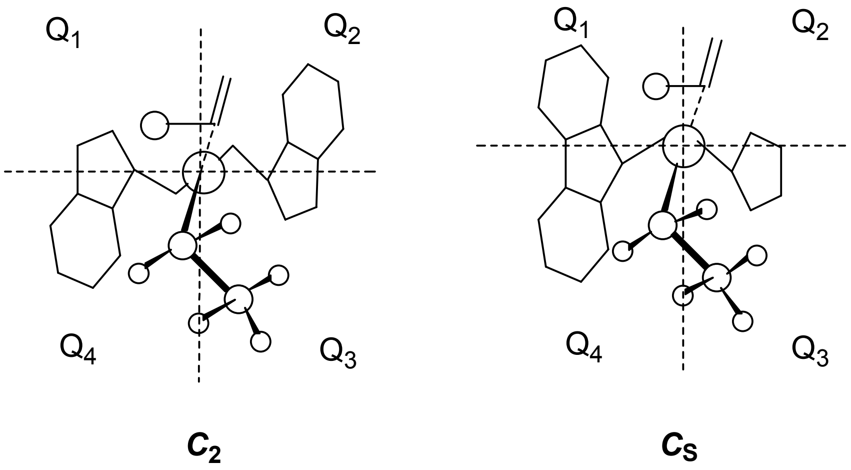


C_{2v} C_2

C_s C_1

Figure 6 For olefin polymerisation reactions, metallocenes may be divided in to four main point-groups, examples of each are shown here.

This work has been confirmed by experimental studies. Recently, Sacchi, Brintzinger and co-workers have shown that there is no stereocontrol over the first inserted monomer unit, even for metallocenes that produce highly isotactic polypropylene.[114] This work corroborates the earlier experimental findings of Zambelli[115] and Pino.[116] Zambelli found that insertion of 1-butene into a Ti–CH_3 bond is partially enantioselective, whereas that of propene is not selective at all.



C_2 C_s

Figure 7 The growing polymer chain always occupies the least congested quadrant. Non bonded interactions with the chain forces a trans orientation of the monomer R-group.

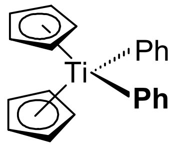
Researchers have exploited these rules outlined here to tailor catalysts for specific purposes. These modifications made to catalysts to improve their polymerisation characteristics are discussed in the next two sections.

3.4. The Effect of Ring Substituents

3.4.1. Unbridged Metallocenes

The first metallocenes used to synthesise polyolefins were unbridged metallocenes. In these complexes both cyclopentadienyl-type ligands rotate freely about the metal–ring centroid axis. As a result of this phenomenon, these catalysts are achiral and do not polymerise propene in a stereospecific manner. If however specific modifications to the catalyst are made or the polymerisation conditions are altered, then control of polymer tacticity can be achieved. An example of the latter was the use by Ewen of the metallocene Cp_2TiPh_2 (**13**) to polymerise propene to isotactic propene at temperatures below –30°C.[11,117] At these low temperatures the catalyst exhibited chain-end control over the polymer formed. Similar results were achieved by Erker and co-workers when employing substituted bis-cyclopentadienyl metallocenes in the polymerisation of propene, also at low temperatures.[118-122]

Enantiomorphic-site control of propene has been accomplished by using appropriate ring substituents. However, low temperature ($T_p < 0^{o}C$) polymerisations are generally still required to achieve this result. By substituting the cyclopentadienyl ring protons with a chiral *tertiary* alkyl substituent, Erker was able to synthesise a double stereodifferentiating catalyst, $(CpCHMePh)_2ZrCl_2$ (**14**).[118] At polymerisation temperatures of between –33 and –79°C this catalyst is able to produce polymer due to both chain-end and catalytic-site control. The majority of the polymer (>65%) is under the former control mechanism. Erker later extended this idea to bis-indenyl catalysts.[123] The polymerisation of propene by (1-neoisomenthyl-Ind)$_2$ZrCl$_2$ (**15**) resulted in the majority (>80%) of the isotactic polypropene being formed through catalytic-site control. It was rationalised that enantiomorphic-site control existed when the rotation of the ligands placed the catalyst in a C_2-conformation, which created a chiral entity. A C_1-conformation of the catalyst on the other hand resulted in chain-end control of the polymerisation reaction at low temperatures. The rotation of the ligands is obviously retarded by the presence of the bulky substituents as most of the polymer produced was isotactic.



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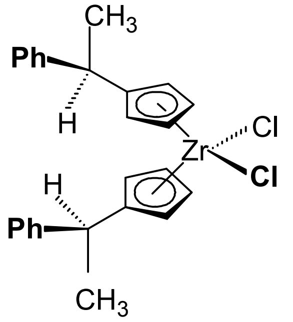

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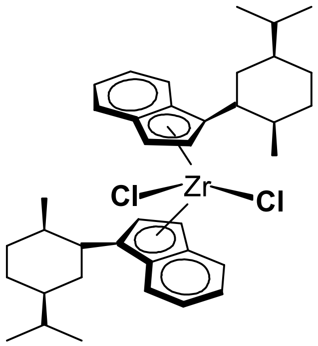

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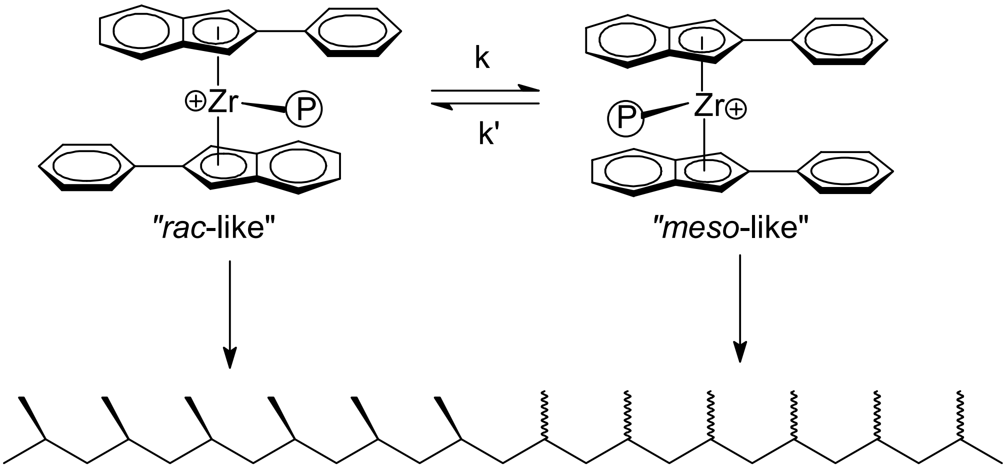
Waymouth has taken this idea one step further. Bulky substituents on the 5-membered ring of indenyl ligands slowed down the rotation of the rings at ambient temperatures.[124-138] In this way both the "*rac*-" and "*meso*-like" structures (Scheme 13) had finite lifetimes, with the polymerisation of propene occurring in *both* these arrangements. When the metallocene was in the "*rac*-like" conformation, isotactic polymer is formed, whereas the "*meso*-like" conformation polymerises polymer in an atactic fashion. The microstructure of this polymer thus consisted of blocks of isotactic and atactic polymer in the same chain, generating an elastomeric polymer.



Scheme 13 By oscillating between between "*rac*-like" and "*meso*-like" conformations, Waymouth's catalyst can produce blocks of isotactic and atactic polymer in the same polymer chain.

Unbridged catalysts are generally used in the polymerisation of ethene, with the simplest metallocenes proving to be most effective for these polymerisations. Janiak has shown that activities suffer a marked decrease as soon as the cyclopentadienyl ligands become highly substituted.[139,140] Activities were found to decrease according to the following series: Cp_2ZrCl_2 (**2**) > $(CpMe_4)(Cp)ZrCl_2$ > $(Cp^*)(Cp)ZrCl_2$ > $(CpMe_4)_2ZrCl_2$ > $(Cp^*)_2ZrCl_2$. Mono-substituted catalysts containing simple alkyl groups (methyl, ethyl, *iso*-propyl and trimethylsilyl) do however have higher activities than **2**.[141-146] Adverse steric-effects associated with ring substituents are even more pronounced when Ti, which has a small atomic radius, is used.[90]

3.4.2. Bridged Metallocenes

One of the most successful approaches to catalyst design has been the use of *ansa*-metallocenes.[3] The most effective *ansa* polymerisation catalysts have a short bridge joining the π-ligands, which pull the ligands back and create a more open site for polymerisation to occur. The bridge also restricts excessive rotations about the M–Cp_c (Cp_c = centroid of the five-membered ring) vector. The effect of different bridges on polymerisation behaviour will be discussed in Section 3.5.

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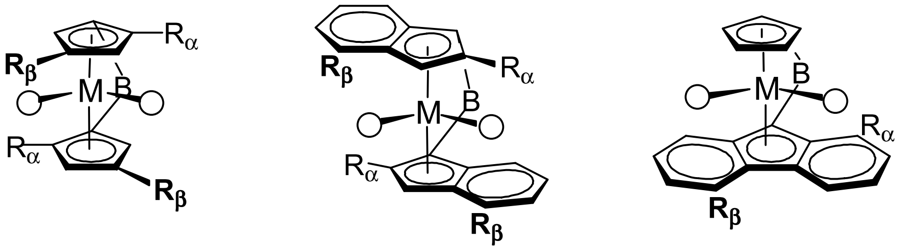
[3] The prefix *ansa* is derived from Latin for "bent handle".

Over the past two decades it has been established that a particular ligand substitution pattern can generate high activity, stereoregularity and specificity of monomer insertion during a polymerisation reaction. What is remarkable is that this simple rule holds true for cyclopentadienyl, indenyl and fluorenyl ligands as well as catalysts that have different symmetries. Examples to indicate this control are discussed below.

Placement of suitable substituents at the α- and β-positions (2- and 4-positions), with respect to the bridge carbon on the cyclopentadienyl ring, influences the polymerisation behaviour of the metallocene catalysts (Figure 8). In the indenyl and fluorenyl rings, these α- and β-substituents form part of the ring structure.[19,106]



B = Bridge
○ = Halide or alkyl

Figure 8 Depiction of the substituents on the α- and β-positions on the cyclopentadienyl, indenyl and fluorenyl ring moieties.

3.4.2.1. *C*$_2$-symmteric Catalysts

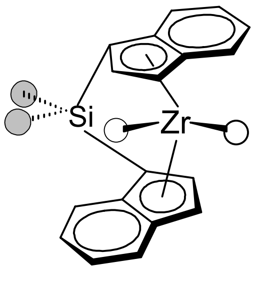
In 1989, Miya *et al.* synthesised a series of metallocene compounds of the formula $Me_2Si[R_nC_5H_{4-n}][R'_nC_5H_{4-n}]MCl_2$ (M = Zr, Hf; R_n, R'_n = Me, ^{t}Bu, 2,4-Me$_2$, 2,3,5-Me$_3$).[86] They found that metallocenes with methyl-substituents in the 2- and 5-ring positions gave polypropene with high molecular weight, melting point and tacticity. However, when a bulky substituent was placed at the 3-position, a drastic decrease in activity was recorded. The reason for this observation is that this position is directly over the active polymerisation site. The substituent therefore blocks the site and hinders the polymerisation reaction. In the following year, Brintzinger *et al.* published a paper containing similar results with catalysts substituted at the 2- and 4-positions.[147] The catalyst with the highest activity and which produces polymer with high molecular weight had a methyl substituent and a *tert*-butyl group at the 2- and 4-positions respectively. Reduced activity and polymer molecular weight was recorded when the methyl group was substituted by a hydrogen atom or the *tert*-butyl by an *iso*-propyl group. An added advantage brought about by the presence of the methyl-substituent is the suppression of 1,3-misinsertions. These results emphasise the importance of the *position* of steric-bulk on the cyclopentadienyl ligand.

Due to their greater Lewis-basicity, indenyl ligands are suggested to be better at stabilising the active polymerisation site. The indenyl framework also lends itself to greater ligand modification, which make further increases in polymerisation activity, polymer melting points and molecular weights possible. The latter two features are particularly important, as the polymer produced by zirconocene catalysts does not compare with that manufactured in commercial plants by heterogeneous Z-N catalysts. Although their hafnocene analogues do produce high molecular weight polypropylene, they are afflicted by low activities.

Two papers by Spaleck *et al.*[97,148] in the early 1990's demonstrated how this "2-4 substitution pattern" can most effectively be put to use in bis-indenyl *ansa*-zirconocenes. The following observations can be made from the results when compared against the reference catalyst *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**16**).[149]

- Substitution of the hydrogen with a methyl group at the 2-position increases polymer molecular weight five-fold and increases isotacticity from 82% to 90% (compound **17**). A bigger group such as ethyl has no significant effect on the polymerisation results.
- An *iso*-propyl substituent at the 4-postion together with the presence of the 2-methyl group, as in **18**, increases the isotacticity to 98%, the molecular weight by a factor of 8 and activity by a factor of 1.8.
- Aromatic groups at the 4-position, such as phenyl and 1-naphthyl, as in **19**, result in *the* most positive impact when compared to the reference compound. The latter, for example, increased the activity by a factor of 4.6 and polymer molecular weight by a factor of 26. There is also a 17% rise in polymer isotacticity to 99%.
- A phenyl group at the 5-postion (**20**) has a deleterious effect on activity with a three-fold decrease being recorded. Although there is 5-fold increase in molecular weight, the polymer isotacticity drops by 3%.
- Benzoannelation at the indenyl 6-membered ring results in metallocene **21** having double the activity of **16** and a nine-fold increase in polymer molecular

weight. This catalyst was independently prepared and tested by Brintzinger and co-workers.[98] Their results corroborated the findings by Spaleck *et al*.



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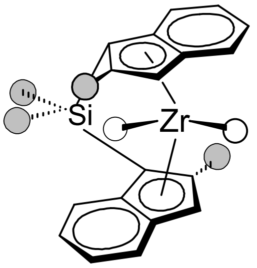

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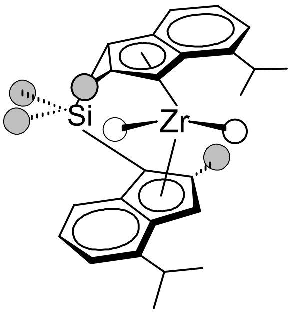

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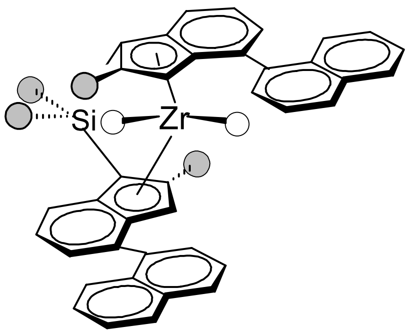

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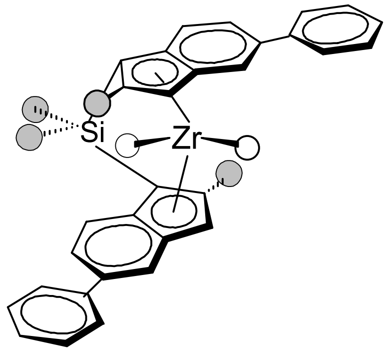

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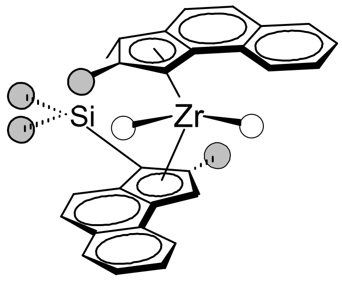


21

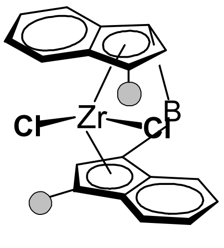
○ = Cl
● = CH_3

The above papers indicate the importance of the presence of *both* the 2- *and* 4-substituents on the ligand framework. As Spaleck stated, the relationship between the two is not incremental, but 100% synergistic.[97] Failure to include any of this substitution pattern into the catalyst structure results in drastic drops in performance.

The reason proposed for the high *activities* are that the alkyl and aryl substituents are electron donating in character. Improved stabilisation of the cationic polymerisation species is therefore possible and thus leads to the higher monomer insertion rates observed. The same ordering in the activity series is also observed when the smaller ethene monomer is polymerised. Steric effects probably also contribute to the protection of one active metal site from another polymerisation species. These bimolecular reactions lead to deactivation.

Both steric and electronic effects were found to be responsible for the high *molecular weights*. Chain termination by β-H transfer to the olefin is blocked by the 2-methyl substituent, which also enforces the rigidity of the metallocene. β-H transfer to the metal is also reduced because of the increased electron density on the active site. Bercaw has demonstrated, through the use of his Cp^*_2ScR model systems, that β-H transfer is facilitated through a four-centred transition state with a positive charge build-up on the β-carbon.[150] More Lewis-basic π-ligands presumably reduce this charge.

Substitution at the 3-position of the indenyl ring has the effect of suppressing 2,1-misinsertions. The polypropylene produced by these catalysts is therefore fully regioregular, examples being the 3-*tert*-butyl (**22**) and -trimethylsilyl (**23**) substituted compounds synthesised by Resconi, Nifant'ev and co-workers.[151-153] These metallocenes are also capable of polymerising propene with moderately high activity and isotacticity. The *tert*-butyl substituent catalyst does however produce a polymer with higher molecular weight and melting point than its trimethylsilyl substituted analogue (% *mmmm* = 91–97 *vs* 80–90 and T_m = 142–158°C *vs* 127–146°C).[151]



● = ^{t}Bu, B = CMe_2 **22**
● = $SiMe_3$, B = CMe_2 **23**

3.4.2.2. C_1- and C_S-symmetric Catalysts

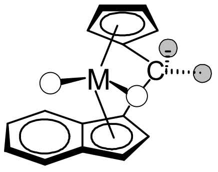
In the synthesis of *ansa*-metallocenes, which have two identical cyclopentadienyl-type ligands, diastereomers are formed due to the prochiral nature of this attaching ligand system. These diastereomeric forms *viz*. *racemic* (*rac*) and *meso* have vastly different polymerisation behaviours. The *rac*-form has C_2-symmetry and usually polymerises propene into isotactic polypropylene. The *meso*-diastereomer belongs to the C_1-point group and, being achiral, forms atactic polymer.[11,154]

A variety of C_1-symmetry *ansa*-metallocenes with mixed cyclopentadienyl-type ligands have been synthesised. Depending on which substituents are used, where they are placed on the ring, the bridge and metal employed, it is possible to influence the tacticity of the polypropylene formed. The metallocenes of the formula B(Cp)(Ind)MCl_2 (B = a bridging unit *e.g.* –CMe_2 or –$SiMe_2$, M = Ti, Zr, Hf) provides some of the most interesting examples to illustrate these points.

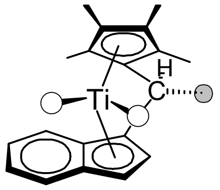
The metallocene Me_2C(Cp)(Ind)$ZrCl_2$ (**25**) is capable of polymerising propene with low tacticity (% *mm* = 35%, T_p = 1°C) and molecular weight even at low temperatures.[89,155] When the metal is replaced by Ti (**24**) or Hf (**26**), polymer with an isotactic (% *mmmm* ~ 70%) microstructure is formed.[155] Rausch *et al.* were able to produce polymer with an elastomeric structure, even at high polymerisation temperatures (T_p = 50°C), when the cyclopentadienyl ligand was replaced with the bulkier tetramethylcyclopentadienyl ligand (**27**).[156] This polymer consists of sections of crystalline isotactic polymer linked by atactic sections (% *mmmm* = 40).

The work by Miyake *et al.* illustrates the importance of the positioning of the substituents on the ligand system.[89] The *threo*-isomer (**28**) of $Me_2C(3\text{-}^tBu\text{-}Cp)(3\text{-}^tBu\text{-}Ind)ZrCl_2$ is ten times more active than the *erythro*- analogue (**29**). The polymer also has a higher isotactic component than that of **29** (% *mm* = 99.6 *vs.* 51.8). Obviously the two β-substituents block one of the polymerisation sites, severely hindering monomer insertions. Similar results were obtained by Yoon *et al*. when metallocenes **30**-**32** were used to polymerise propene.[157] When activated by MAO, **30** and **31** formed a polymer with a low tacticity while **32** formed an atactic polymer. The similarity of the former two structures to the C_s-symmetric B(Flu)(Cp)MCl_2 systems, which will be discussed below, provide a clue as to their polymerisation behaviour.

Ewen and co-workers have performed innovative and useful work in *ansa*-metallocene research. In a series of research papers it was shown how substitution of the C_s-symmetric metallocene Me_2C(Cp)(1-Flu)$ZrCl_2$ (**33**) could change the tacticity of the polypropylene formed from syndiotactic to hemiisotactic to isotactic.



M = Ti **24**
= Zr **25**
= Hf **26**



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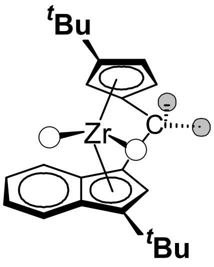
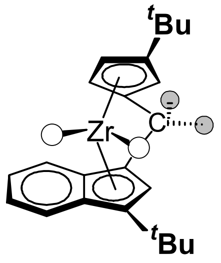
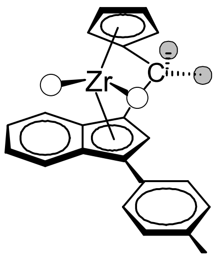


28 (*threo-)*



29 (*erythro-*)



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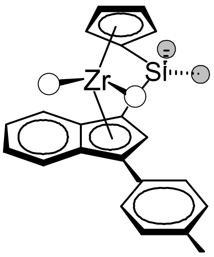

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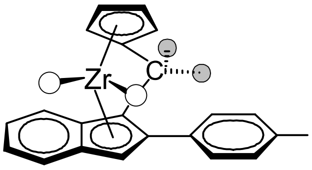
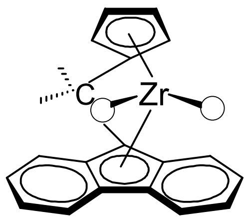


32

○ = Cl
● = CH$_3$

In 1988 Ewen *et al.* published their findings on the discovery of a C_s-symmetric catalyst (**33**) that is capable of producing syndiotactic polypropylene, even at high temperatures (T_p = 70°C).[158,159] This metallocene is achiral due to the presence of an intermolecular mirror plane. The chirality of the molecule is achieved during activation, leaving one co-ordination site vacant and the other methylated by the co-catalyst. During polymerisation, the polymer chain always occupies the least sterically encumbered region of the metallocene, with its α- and β-carbons orientated away from the bulky fluorenyl ligand. Through non-bonded interactions the incoming olefin monomer is then forced to co-ordinate with its methyl group away from the chain, towards the fluorenyl ligand.



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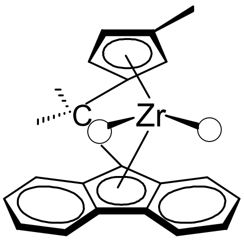

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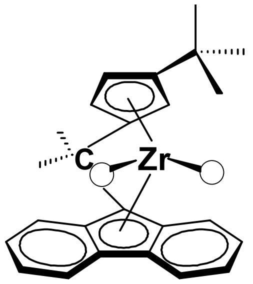

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Modification of the structure of **33** provides a revealing insight into the polymerisation mechanism. In **34**, a methyl group is placed on the cyclopentadienyl ligand above one of the active sites.[160] This removes the mirror-plane symmetry element, confining the compound to the C_1-point group. The resulting polymer from polymerisations employing **34** is hemiisotactic in microstructure. When the attached polymer is on the unhindered side of the molecule, insertion of the co-ordinated monomer occurs in a syndiotactic manner. However, the polymer chain is now forced by non-bonded interactions, when attached to the hindered side, into a conformation that can no longer have any significant effect on the orientation of the co-ordinated monomer. The second insertion therefore occurs in an atactic fashion. One further modification made was the placement of a bulky *tert*-butyl group on the cyclopentadienyl ligand (**35**) resulting in the formation of isotactic polypropylene.[161] When the polymer chain moves to the more crowded metal site, the steric congestion causes it to "skip-back" to the less hindered site. Therefore monomer insertion can only occur from one side of the molecule, resulting in an isotactic polymer being formed.

3.5. The Effect of Bridge Choice

The bridge used to link the π-ligands, also influences the metallocene polymerisation reaction. Linking the cyclopentadienyl moieties together "opens-up" the active polymerisation site to larger α-olefins. Further, by joining the ligands the structure becomes more immobile, presenting a rigid face to the incoming monomer. Lastly, depending on bridge choice, a number of electronic changes can be made to the catalytic species. All these factors influence the polymerisation activity and physical attributes of the polymer produced.

Although a plethora of bridge choices exist, the most effective and widely used are the ethylene, *iso*-propylidene and dimethylsilane spacers. These are depicted in Figure 9, which shows linked bis(indenyl)zirconium dichloride systems. Of these, the dimethylsilyl bridge is the most ubiquitous and has been employed in some of the most effective metallocene polymerisation catalysts.[97,98,148,149,161,162] The ethyl bridge creates a less rigid metallocene, making it less selective for propene polymerisation. The isotacticity, melting points and molecular weights of the polymer it forms is also lower than that made by dimethylsilyl bridged metallocenes.[85,149] These differences are accentuated when even longer bridges are used, as seen by the inactivity of **36** towards the polymerisation of propene. The X-ray crystal structure of **36** reveals that the longer bridge results in one of the indenyl ligands being pushed into a shielding position over the active polymerisation sites.[149]

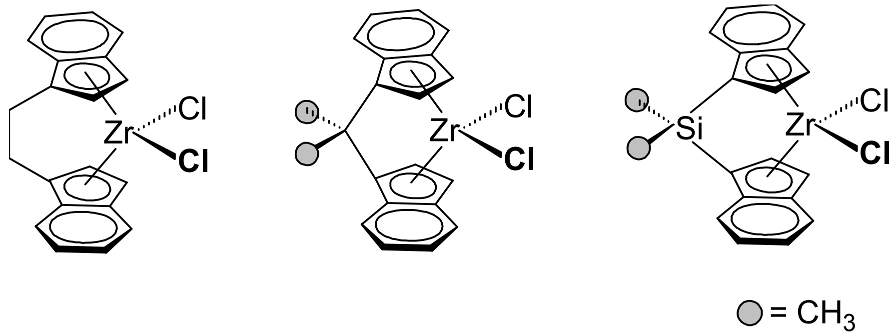
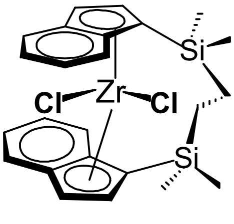


Figure 9 Three main bridging systems exist in *ansa*-metallocenes, namely ethyl, isopropyl and dimethylsilyl bridges.



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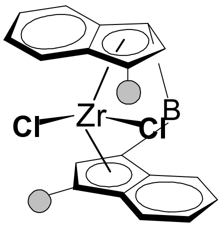
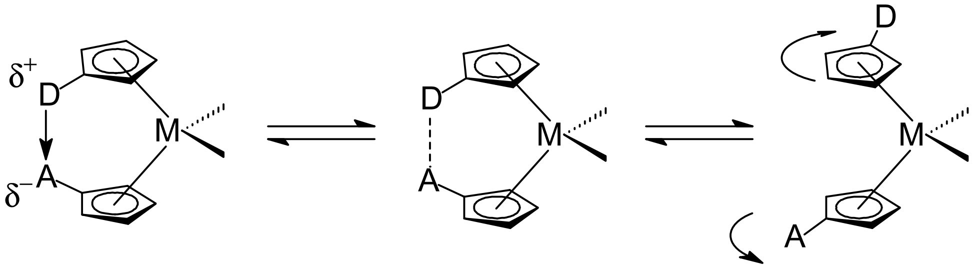
The influence of bridge type has been clearly demonstrated by comparing the results from polymerisation reactions involving various 3-substitued, bis-indenyl metallocenes. As was mentioned earlier, metallocenes substituted at the 3-position polymerise propene in a fully regioregular manner, however, the stereospecificity exhibited by these catalysts is largely dependant on the type of bridge linking the indenyl ligands. The ethyl bridged metallocene Et(3-Me-Ind)$_2$ZrCl$_2$ (**37**) is only capable of producing an amorphous polymer.[151,162] The reason is proposed to relate to the lack of steric differentiation between the methyl and the benzene rings in **37**. This leads to the incoming monomer having no preferential orientation. By introducing a shorter dimethylsilyl bridge and changing the substituent to a *tert*-butyl group Miyake was able to form propene with poor isotacticity (% *mm* = 75.5) and molecular weight (M_w = 5000) at low polymerisation temperatures (T_p = 1°C).[89] However, by changing the bridge to an even shorter *iso*-propyl spacer (**22** and **23**), it is possible to generate metallocenes that are highly stereoselective (% *mmmm* > 90).[151,152] This shorter *iso*-propyl bridge creates a more open metallocene, resulting in a larger bite-angle. This modification, together with the bulky substituent over the active polymerisation site contributes to the higher stereoselectivity of **22** and **23** over **37**. Resconi and co-workers have recently also demonstrated the profound influence that substituting the methyl groups on the *iso*-propyl bridge of **22** with hydrogen atoms has on improving the polymerisation behaviour of the resulting catalyst.[153] The polypropylene generated by $H_2C(3\text{-}^t\text{Bu-Ind})_2ZrCl_2$ (**38**) has a higher molecular weight, melting point and isotacticity than that formed by **22**.



● = Me, B = C_2H_4 **37**
● = ^{t}Bu, B = CH_2 **38**

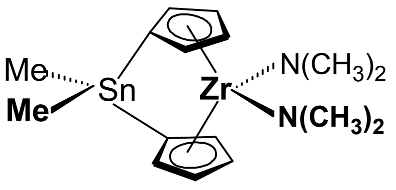
An innovative bridging system, consisting of a donor group (*e.g.* O, N, P) on one ligand and an acceptor group (*e.g.* B, Al) on the other, was recently published.[163] The ligands are therefore capable of linking creating a C_2-like *ansa*-system, but may still disconnect and rotate (Scheme 14). Depending on the polymerisation temperature and the donor-acceptor pair used, it is possible to obtain a wide variety of polymers.



Scheme 14 Donor-acceptor metallocene are capable of equilibrating between bridged and unbridged systems.

Apart from the Si and C based bridging systems a variety of other main-group elements have found their way into the synthesis of Group 4 metallocenes. These include As,[164] B,[164-167] Ge,[168-170] P[171,172] and Sn.[173] These bridging atoms, together with the groups attached to them introduce totally new steric and electronic parameters to metallocene catalysts. Herrmann's Sn-bridged metallocene (**39**), for example, is capable of polymerising ethene more efficiently than its Si-bridged analogue.[173]

A number of other creative uses of bridging systems have appeared in the literature. The use of stereogenic bridges, to preclude the formation of diastereomers, has attracted much interest and will be discussed in greater detail in Section 4 of this review. Lastly, during the course of Alt's investigations into fluorenyl compounds, he has managed to synthesise a number of metallocenes with alkenyl substituents attached to a bridging atom (*e.g.* **40**).[23,174] During a polymerisation reaction these metallocenes themselves then get co-polymerised into the polymer chain in a "self-immobilising step". This heterogenisation of the catalyst prevents many of the problems of using unsupported metallocenes in commercial reactors.



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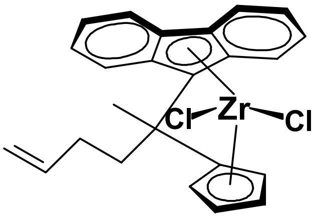

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4. Metallocene Synthesis: Resolving the Problem of Diastereomers

The general procedure followed in the synthesis of metallocenes is quite simple: the ligand is deprotonated by a metallic base (*e.g.* KH or ^{n}BuLi) and then mixed with a metal halide (*e.g.* $ZrCl_4$) in an appropriate solvent. As most of the *ansa*-ligands are prochiral the final metallation step can give rise to three diastereomers *viz.* two *rac* and one *meso* diastereomer. The former two are generated when the two ligand faces attach to the metal in either a *si*, *si* or *re, re* fashion. The latter diastereomer however forms when there is a *re, si* attachment. Unfortunately only the *rac*-product is usually capable of polymerising α-olefins into commercially acceptable materials with the *meso*-diastereomer responsible for producing atactic oils and waxes. The unwanted product has to therefore either be separated from the final product or be precluded in the synthesis step. This conundrum has generated a great deal of thought amongst researchers and the main solutions proposed to resolve this issue is discussed below.

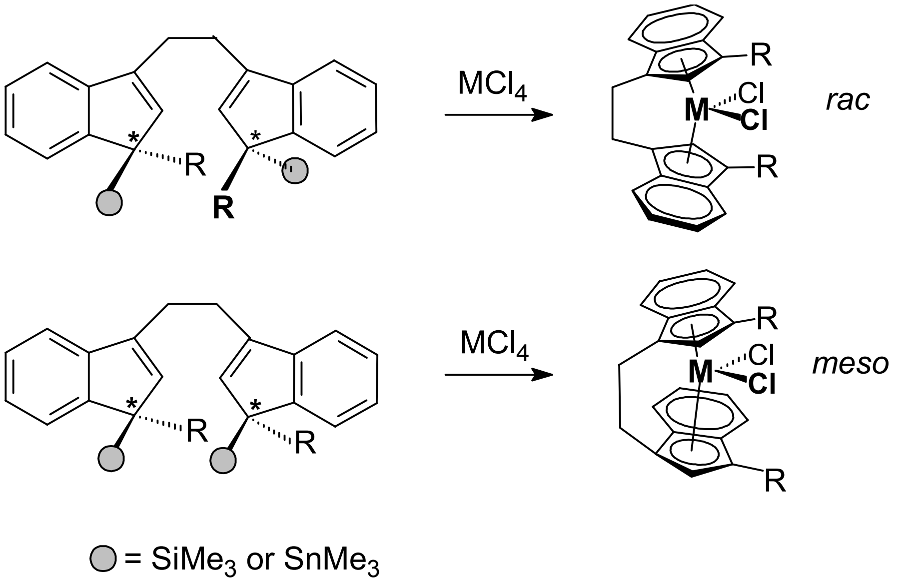
There exist three broad strategies which have been employed to maximise the yield of the *rac*-isomer. These are:

- Synthetic strategies: these deal with the details of the experimental procedure such as the reaction conditions and reagents used.
- Ligand strategies: the design of unique ligands that only give the desired diastereomer or at least maximises its yield.
- Separation strategies: the employment of techniques that extract the desired compound from a product mixture.

4.1. Synthetic Strategies

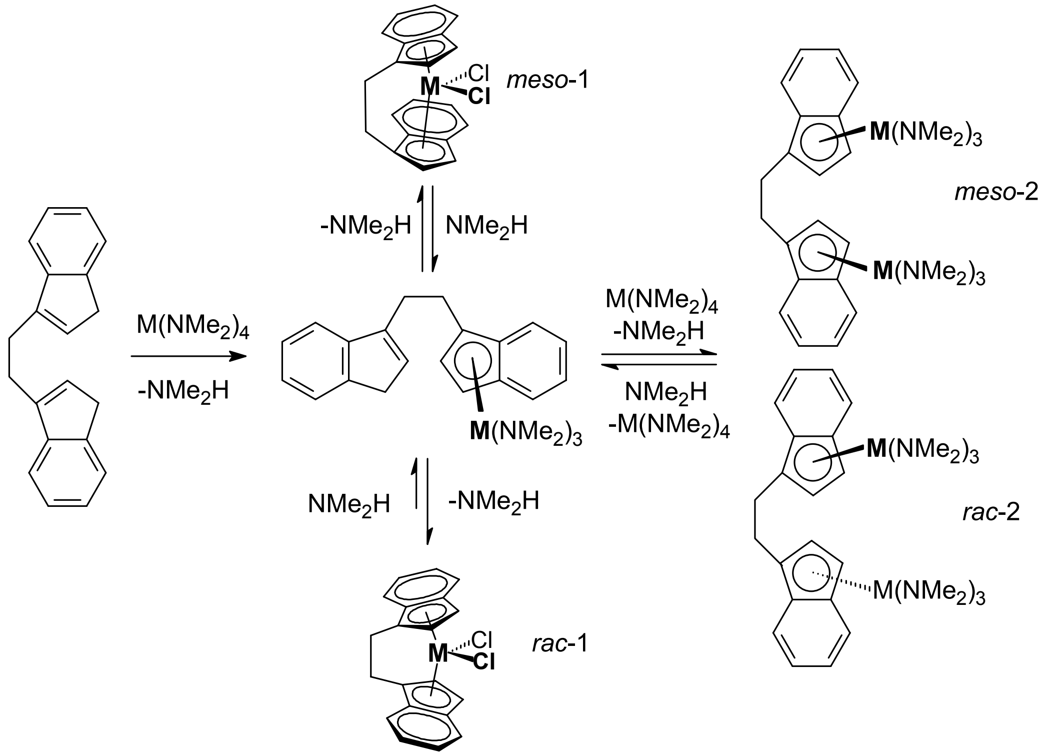
The original synthesis procedures used to generate metallocenes such as $Et(IndH_4)_2MCl_2$ (Ind = 1-Ind, 1-IndH$_4$; M = Ti, Zr) proceed with low overall yield.[10,175] For example, Collins found that the yield of the *rac*-isomer could be improved by the slow, simultaneous addition of the lithiated ligand and $MCl_4.(THF)_2$ (M = Ti, Zr) to a third reaction vessel using high dilution.[176-178] In doing this, the formation of polymeric products are minimised and the formation of the *rac*-diastereomer was favoured over that of the *meso*-isomer (*rac:meso* = 5–6:1). The reaction is not predictable and yields can vary between 30 and 80%. Buchwald published a variation on the latter procedure, except that the base KH was used to deprotonate the ligand instead of ^{n}BuLi.[179] Although this leads to a higher yield of product (40-50%), the selectivity of the reaction decreased (*rac*:*meso* = 2:1), as it required a more difficult separation step.

A novel method for introducing ligands to the metal in a diastereoselective manner is by use of Sn and Si reagents in the transmetallation step. Silylated or stannylated versions of the ligands can easily be generated in almost quantitative yields. These metals must associate with one particular side of the ligand. If this attachment is *syn*, the ligand will attach to the metal halide (MCl_4, M = Ti, Zr, Hf) to give the *meso*-diastereomer. Conversely, employment of the *anti*-ligand will generate the *rac*-diastereomer (Scheme 15). This procedure has been employed by several researchers in the synthesis of bridged cyclopentadienyl and indenyl metallocenes.[151,180-185]



Scheme 15 The asymmetric synthesis of ansa-metallocenes can be rendered diastereoselective by reacting the stannylated or silylated versions of the ligands with the metal chloride.

The research work of Jordan has provided researchers with an extremely useful diastereoselective synthetic route. The procedure involves the reaction of the ligand with $M(NMe_2)_4$ (M = Zr, Hf) in a reversible amine-elimination pathway (Scheme 16).[186-191] It was found that at the beginning of the reaction the two diastereomers formed at comparable rates. However, the reversibility of the metallation/amine-elimination steps allows the thermodynamic product, *rac*-1, to preferentially form as the reaction progresses over time. Jordan has recently also investigated the synthesis of metallocenes by the reaction of aluminium *ansa*-bis(indenyl) compounds with these metal amides.[192] Unfortunately, the conventional salt or amine elimination methods are more efficient routes towards the synthesis of *ansa*-metallocenes.



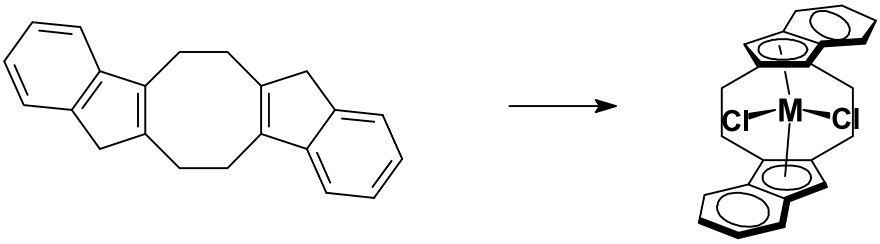
Scheme 16 The amine-elimination reaction developed by Jordan and co-workers favours the formation of the thermodynamically favoured *rac*-diastereomer, *rac*-1.

4.2. Ligand Strategies

The second approach taken by researchers to maximise the yield of the desired *rac*-isomer involves constructing ligand systems that either make it difficult for the unwanted *meso*-diastereomer to form, or avoids their synthesis altogether. For example, in the former case it has been found that in the synthesis of bis-cyclopentadienyl *ansa*-metallocenes, the *rac*-configuration can be favoured by introducing substituents in the α- *and* β-ring positions. The *rac:meso* ratio can be raised from 1:1 in the mono-substituted ligands to ratios of between 2–6:1 for their disubstituted counterparts.[193-196]

Appropriate bridge-substituents have also been shown to increase the yield of the *rac*-diastereomer. By using a bulky germylene bridge, Chen *et al.* were able to obtain a *rac:meso* ratio of ~7:1 for the metallocene [(1,2,3,4-tetraphenyl-1,3-butadiene-1,4-diyl)-Ge](1-Ind)$_2$ZrCl$_2$.[169] Similarly, Huhn *et al.* were able to increase the yield of *rac*-R,MeSi(2,4-Me$_2$-Cp)$_2$ZrCl$_2$ by changing the bridging R-group from methyl to vinyl.[197]

The *rac:meso* isomer problem can also be solved by using doubly-bridged π-ligands that can attach to the metal to only give one diastereomer. This depends on the construction of the ligand.[198-203] An example of this is provided in Scheme 17, the route that Halterman followed to synthesise *rac*-bis-indenyl titanium and zirconium dichlorides. The design of the ligand ensures that only one isomer can form once one of the ligands has attached to the metal.[202]



Scheme 17 The use of doubly-bridged indenyl ligands allows the synthesis of only one diastereomer, thus doing away with tedious separation procedures.

An innovative design-methodology has been developed by the research groups of Bosnich and Haltermann.[204-212] By reacting chiral ligands, which consist of two cyclopentadienyl-type groups linked by a stereogenic bridge, they have been able to exclusively obtain one diastereomer. Examples of metallocenes synthesised using these ligands are shown in Figure 10.

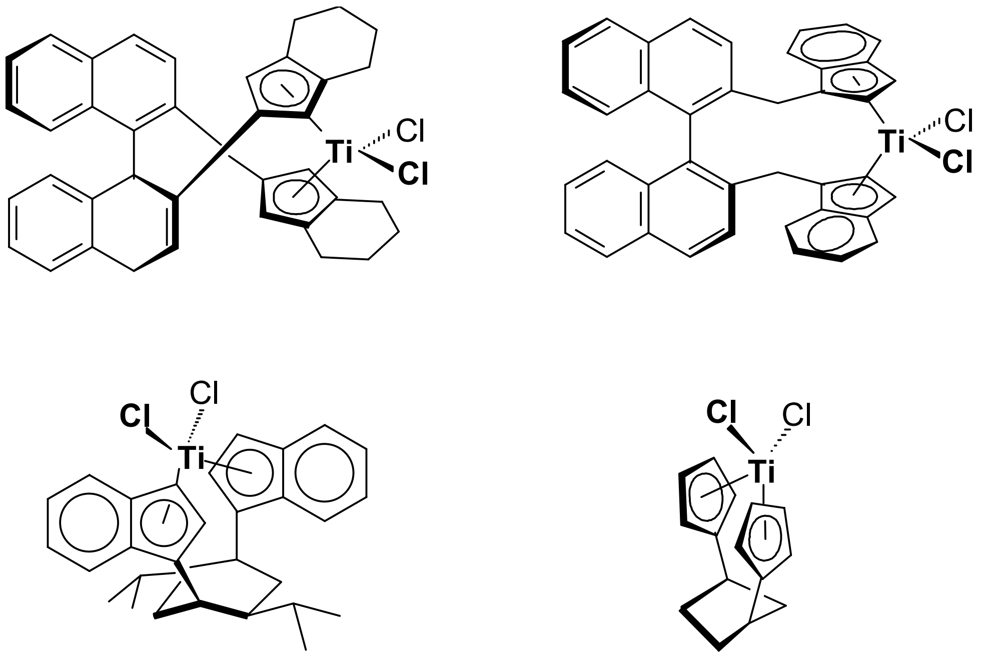


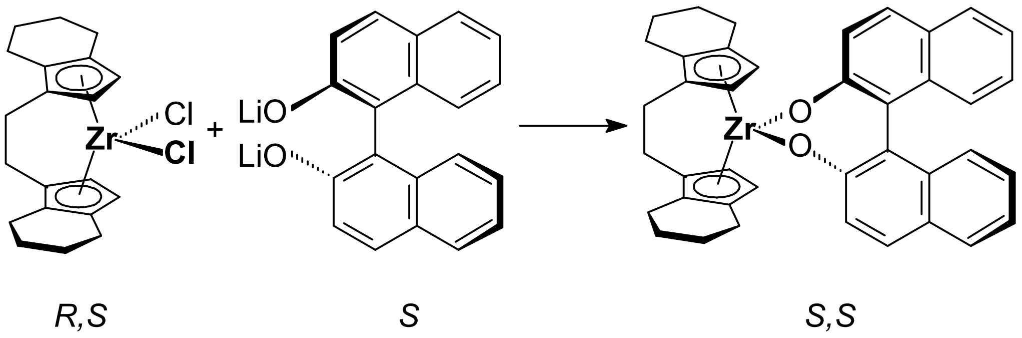
Figure 10 The use of chiral ligands in the synthesis of ansa-metallocenes ensures that only one diastereomer is formed.

4.3. Separation Strategies

As the synthesis of *ansa*-metallocenes invariably results in the generation of at least some of the unwanted *meso*-diastereomer, techniques have had to be developed to separate these from each other. The most common route followed is exploitation of solubility differences, if there are any, between the different diastereomers. Thus solvent-extraction or fractional crystallisations can be used to effect separation, the latter method being applied in the synthesis of nearly all metallocenes.

Separation by chromatography has not been particularly successful due to the decomposition of the metallocenes over silica or alumina. Collins[213] and Erker[214] have however successfully employed the use of deactivated (silanated) silica gel, to purify metallocenes with minimal decomposition.

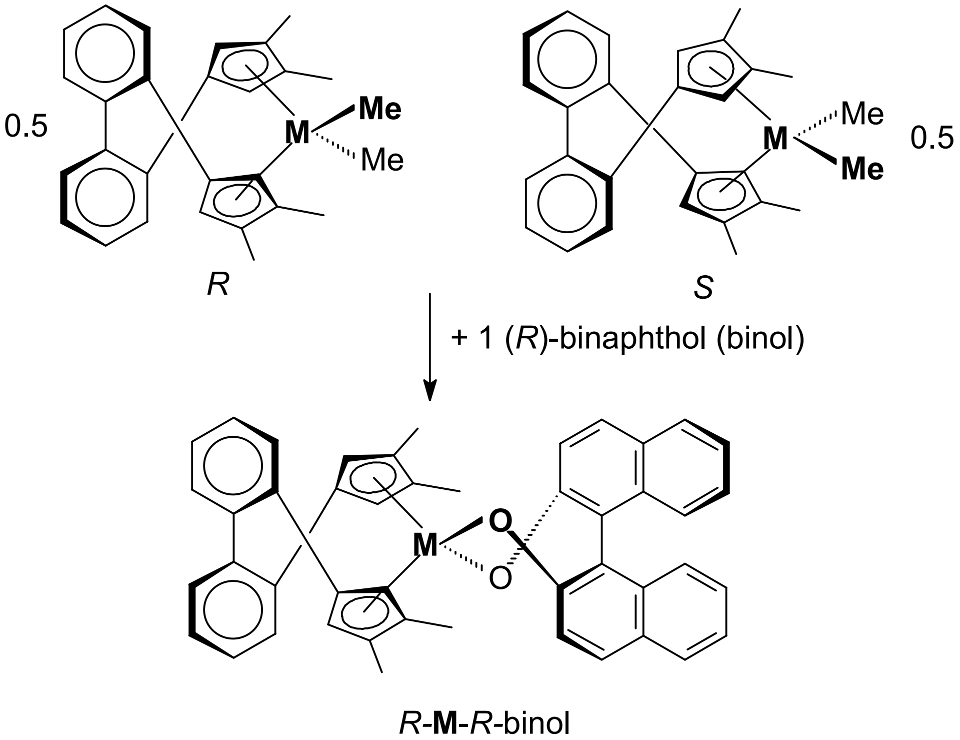
Group 4 metallocenes have become useful tools in asymmetric-catalysis reactions. However, optical resolution of the *racemic* products, derived from their synthesis, is required before they can be successfully deployed in these organic transformations. This resolution of the desired diastereomer is usually accomplished through an enantioselective reaction with a chiral binaphthol (Scheme 18).[10,179,215] Unfortunately this process is inefficient as not more than half of the racemate can be retrieved (the *R,R*- and *S,S*-*rac* diastereomers are usually formed in a 1:1 ratio during synthesis).



Scheme 18 Resolution of the racemic diastereomers can be achieved by reaction with the appropriate lithiated chiral binaphthol.

Brintzinger's research group has managed to convert a *meso*- to the *rac*-diastereomer by a photoisomerisation technique using a high-pressure mercury lamp. The metallocene *meso*-Et[IndH$_4$]$_2$TiCl$_2$ was converted to its *rac* analogue within three hours using this method.[10] It was also found that the *rac* and *meso* enantiomers of Me$_2$Si(2-Me-4-R-Cp)$_2$ZrCl$_2$ (R= ^{t}Bu, Ph) could be transformed between each other to obtain photostationary mixtures with *rac:meso* ratios close to 1.[216] Performing the photoisomerisation in the presence of the appropriate chiral binaphthol trapped the desired *rac*-form. Unfortunately, this technique is restricted to very few *ansa*-metallocenes.

Lastly, it has recently been shown by Brintzinger *et al.* that asymmetric transformations can occur is certain systems.[217] By reacting a 1:1 *R*- and *S*-mixture of a biphenyl-bridged metallocene with *R*-binaphthol, only the *R,R*-product is obtained indicating that an *epimerisation* of the *S*-diastereomer had occurred (Scheme 19).



Scheme 19 The reaction of (*R*)-binaphthol with the *R*- and *S*-biphenyl bridged metallocenes only give the *R*,*R*-product indicating that epimerisation of the *S*-diastereomer had occurred.

5. Quantification of Steric Effects

The discussion on metallocene design highlighted the significance of structural changes and the effect they have on catalyst polymerisation behaviour. Of particular importance is the steric influence that different ligands, especially the substituted cyclopentadienyl ligands, have on the active polymerisation centre. It is therefore useful to be able to quantify various steric parameters associated with the ring system, which may help in the design of better metallocene catalysts. The methods used to measure these steric parameters may be divided in two groups *viz*. (i) those which measure the size of the substituted cyclopentadienyl ligand and (ii) measurements that assess the size of “gaps” associated with a metal centre that accommodate the polymer chain and reactant molecules. Below are described methods to quantify steric effects that have been developed for metallocene catalysts.

5.1. Ligand Size Measurements

To measure the impact of a particular ligand on the active polymerisation centre it is necessary to measure the ligand size from the perspective of the metal. These measurements may be accomplished by way of three methodologies *viz.* the Tolman cone angle, analytical solid angle and numerical solid angle.[218-227].

The Tolman cone angle (θ) is the sum of the half vertex angles for *n* unsymmetrical groups in a ligand, multiplied by two. (Figure 11 and Equation 1).[218,219] The half-vertex measures the largest angle from the metal to the outer van der Waals radius of a particular substituent.

$$\theta = \frac{2}{n}\sum_{i=1}^{n}\theta_i/2 \tag{1}$$

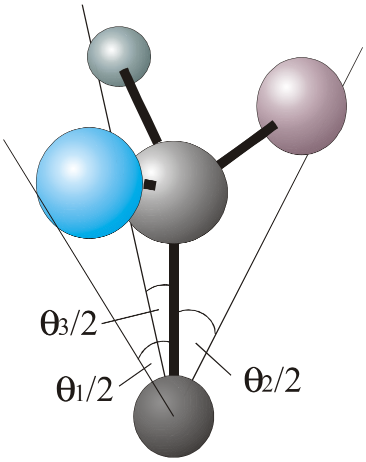


Figure 11 The Tolman cone angle methodology involves the measurement of the half-vertex angle for each substituent in an unsymmetrical ligand.

Thus, in the Tolman cone angle calculation for a cyclopentadienyl ligand, the half-vertex angle to each of the five cyclopentadienyl carbon atom substituents is measured. Maitlis and Tolman were the first to report details on the use of the Tolman cone angle concept to measure the size of cyclopentadienyl ligands.[219,228]

In its simplest form, the equation used in the computation of the analytical solid angle (Ω) is defined by the integral given in Equation 2. The analytical solid angle is therefore calculated in the integrand by subtending a vector **r** (whose magnitude is *r*) from an origin position to a point on a surface, whose area is *dS*. It is more easily visualised as the surface area of the ligand shadow projected onto a unit sphere (Figure 12). If the ligand shadow covers the entire sphere, the solid angle will be 4π steradians. Steradians (sr) are usually not the unit of choice for expressing the size of a ligand. Conversion from steradians into the angle of a cone, which covers the same area, allows this measurement to be described in degrees (Equation 3).[221-227]

$$\Omega = \int_S \frac{r \cdot dS}{r^3} \tag{2}$$

$$\theta/^{\circ} = 2\arccos\left[1 - \frac{\Omega(\mathrm{sr})}{2\pi}\right] \tag{3}$$

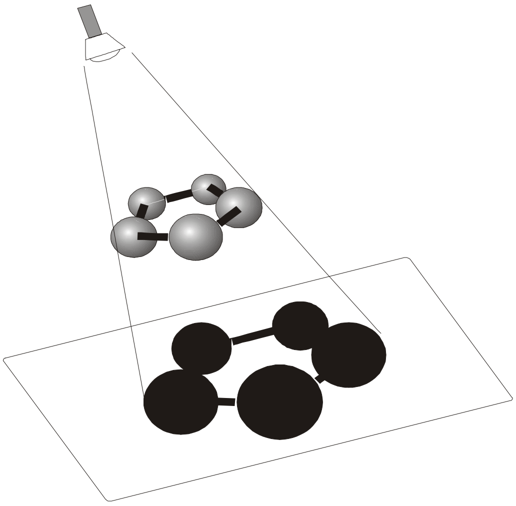


Figure 12 The analytical solid angle is calculated by reflecting the shape of the ligand onto a unit sphere and calculating the size of that shadow.

The numerical solid angle (Ω_N) can be considered as a compromise between θ and Ω measurements. In this calculation a *non-circular cone* is traced around the outer van der Waals radius of the ligand being measured.[220] Figure 13 demonstrates how this cone is measured by rotating an axis through ϕ degrees, thereby measuring the semi-cone angle, $\theta/2$, around the group being studied (Figure 13 and Equation 4). As with the solid angle, the values derived from this calculation can be converted into the angle of a cone using Equation 3.

$$\Omega_{\mathrm{N}} = \int_{\phi=0}^{2\pi} (1 - \cos\frac{1}{2}\theta)d\phi \tag{4}$$

The results from the steric measurements of various mono-substituted cyclopentadienyl and indenyl ligands using these three calculations are collected in Tables 2 and 3 respectively.[146,229] It should be noted that atomic co-ordinates obtained from the X-ray crystallographic studies of the respective bis(R-cyclopentadienyl)zirconium dichloride compounds were used in the steric measurements listed in Table 2. As no X-ray crystallography data is available for most of the bis(R-indenyl)zirconium dichloride metallocenes, these structures were constructed from the average structural parameters listed in the papers by Allen, Orpen and co-workers.[230,231] The Zr–Cp_{cen} length was however set at 2.239 Å, the average value for similar structures obtained from the Cambridge Structural Database.

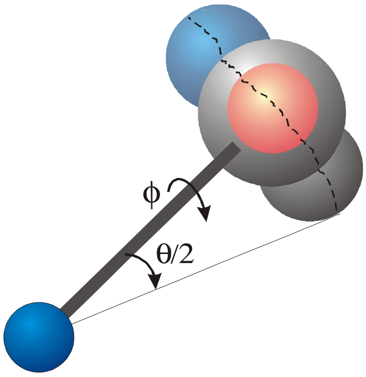


Figure 13 Representation of the ligand angular profile used to create a non-circular cone.

Table 1 Table of Steric Measurements for a Set of (C_5H_4R)–Zr Fragments.[a]

R	θ/° [b]	Ω/° [c]	Ω_N/° [d]
H	135	117	120
Me	140	122	125
Et	143	126	129
*ⁱ*Pr	143	128	130
*ᵗ*Bu	148	133	135
$SiMe_3$	146	131	134
CH_2Ph	146	129	131
CMe_2Ph	147	136	136

[a] The size of the C_5H_4R ligands were determined from the perspective of the zirconium nucleus. All the measurements were derived using Zr–Cp_{cen} distances obtained from the crystal structures of the corresponding $(CpR)_2ZrCl_2$ metallocenes.[146] The values are thus different from those listed in earlier literature tables.[145]

[b] The Tolman cone angle.[218,219]

[c] Solid angle calculated using analytical methods.[221]

[d] Numerical solid angle.[220]

Table 2 Steric measurements for a set of 1- and 2-substituted (**R**-Ind)–Zr fragments. [a]

R		Measurement Technique		
1-R	2-R	θ / ° [b]	Ω_N / ° [c]	Ω / ° [d]
H		143	127	123
	Me	150	135	131
Me		150	135	130
	Et	149	136	131
Et		149	136	133
^{i}Pr		152	138	134
^{t}Bu		163	147	144
	$SiMe_3$	164	148	144
$SiMe_3$		163	147	144
	Ph	150	139	134
Ph		152	139	134
	Bz	149	136	133
Bz		149	136	132
	(1)-Naph	150	140	136
(1)-Naph		152	139	133

[a] The size of the R–Ind ligands were determined from the perspective of the metal. The Zr–Cp_{cen} distance was set at 2.239 Å.[229]

[b] The Tolman cone angle.[218,219]

[c] The numerical solid angle.[220]

[d] The solid angle calculated using analytical methods.[221]

As can be seen from the tables, there are large differences between the values obtained by the different calculations. The question therefore remains, which calculation should be used?

The two solid angle measurements are considered an improvement over the Tolman cone angle as the latter assumes cylindrical symmetry of the ligand and ignores spaces between the atoms in a ligand. The analytical solid angle circumvents this problem by taking the actual shape of the ligand into account. A possible shortcoming of this latter approach is that the solid angle subtracts out the spaces *within* the molecule itself. This is intuitively incorrect since when we refer to the "steric effect of a group", we are usually referring to its steric bulk and the effect of *this size* on a reaction. Spaces *within* this group are not considered to have any impact on the reaction unless the ligand is flexible with steric pressures altering its size *e.g.* in the case of a cyclohexyl group. The numerical solid angle has therefore been designed so as not to count these internal spaces and to rather trace the vertex outline of the ligand at a set distance from a point of observation. Thus, unlike the Tolman cone angle where only the maximum value for each group is taken into consideration, the entire surface of the group is measured in this latter calculation by use of a *non-circular* cone.

However, in the case of a *rapidly rotating ligand*, as in the case of non *ansa*-metallocenes, the empty spaces between the substituents/atoms of a ligand are inaccessible to an external chemical entity. The solid angle calculations, which remove these spaces, are therefore inappropriate in these types of complexes and the cone generated by the Tolman cone angle should be used.

It is also possible to use these three calculations in the measurement of ligand profiles. Here the size of a ligand is measured as a function of distance from the point of measurement.[222,223,226,227] Figure 14 illustrates the ligand profiles of a *tert*-butylcyclopentadienyl ligand whose ring centroid is positioned 2.202 Å from a metal atom.[146] This diagram also illustrates the differences between the different calculation methodologies.

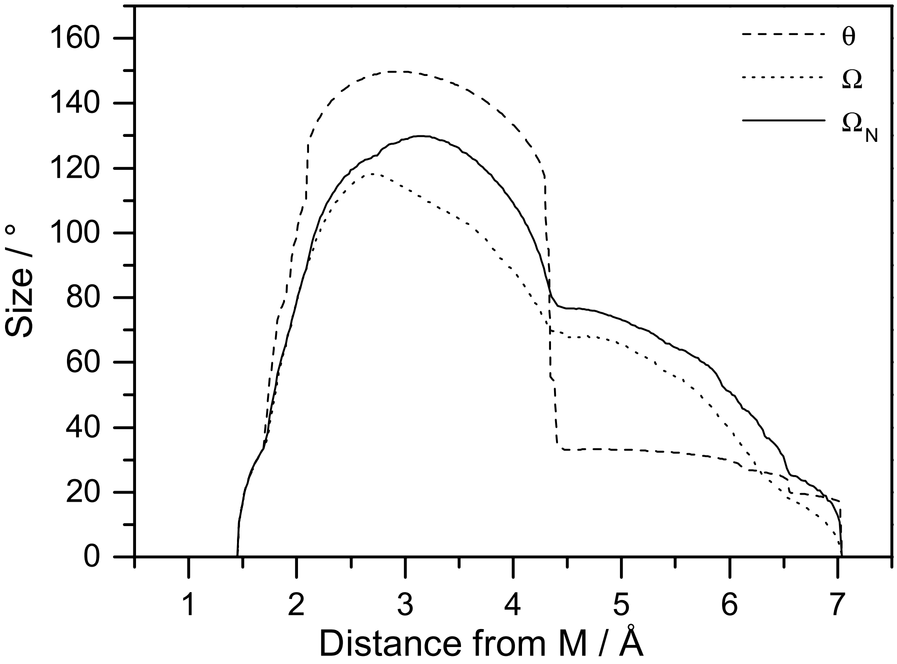


Figure 14 Ligand profile plots for a *tert*-butylcyclopentadienyl ligand positioned 2.202 Å from the point of measurement.

5.2. Measurements of Molecular Spaces

Brintzinger *et al.* have defined two parameters that are useful in quantifying the spaces within the molecular structure of a SCC.[232,233] The first is the co-ordination gap aperture (cga), which measures the amount of space available to a reactant molecule approaching the active polymerisation centre on the metal. The calculation measures the angle formed by two planes, through the metal, which touch the inner van der Waals radii of the β-substituents (Figure 15). These substituents are orientated into a conformation that maximizes the aperture angle. The second measurement is the lateral extension angle, which measures the angle formed between two planes, also through the metal, but which touch the van der Waals radii of the two α-substituents on either side of the complex (Figure 16).

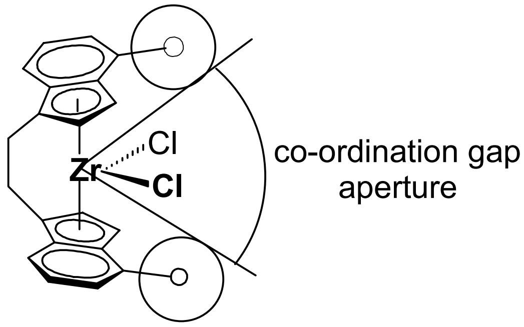


Figure 15 The co-ordination gap aperture is measured as the largest possible angle between the inner van der Waals surfaces of the β-substituents on the 5-membered ring.

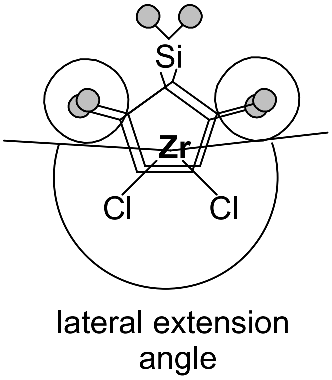


Figure 16 The lateral extension angle is the angle formed between the two vectors, originating at the metal, which touch the van der Waals outline of the two α-substituents on either side of the complex.

By using the cone angles of the cyclopentadienyl ligand (α) and bending angle (β) at the zirconium atom, Janiak and co-workers were able to calculate the co-ordination gap aperture for a series of substituted bis(cyclopentadienyl)zirconium dichloride metallocenes according to Equation 5 (Figure 17)[140]:

$$\text{cga} = 360^{\circ} - \alpha_1/2 - \alpha_2/2 - \beta \qquad (5)$$

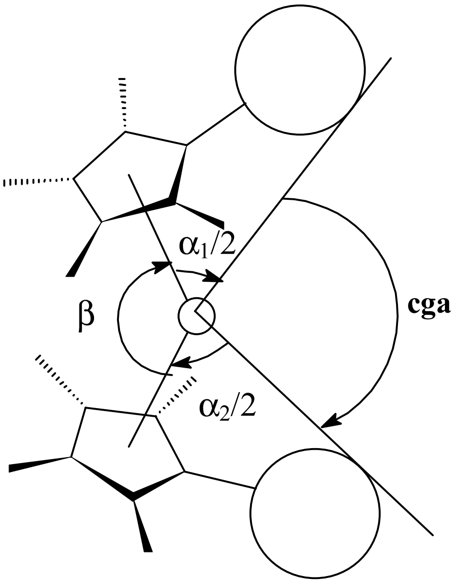


Figure 17 The co-ordination gap aperture (cga) can be calculated by knowing the bending angle (β) of the metallocene and the half cone angle ($\alpha/2$) of its cyclopentadienyl ligands.

The results from these calculations are collected in Table 3. This data was used to rationalise the ethene polymerisation behaviour of these metallocenes, with a decreasing co-ordination gap aperture being found to lead to a drop in polymerisation activity.[140]

Table 3 Co-ordination gap aperture measurements for metallocene compounds.[a]

Compound	cga / °
Cp_2ZrCl_2	92[b]
$(CpMe_4)(Cp)ZrCl_2$	76
$(CpMe_4)_2ZrCl_2$	62
$(C_4Me_4P)(Cp)ZrCl_2$	75
$(C_4Me_4P)_2ZrCl_2$	58
$(Cp^*)(Cp)ZrCl_2$	75
$(Cp^*)_2ZrCl_2$	55
$(^tBuCp)(Cp)ZrCl_2$	74
$(^tBuCp)_2ZrCl_2$	58
$(1,3\text{-}^tBu_2\text{-}Cp)(Cp)ZrCl_2$	66
$(1,3\text{-}^tBu_2\text{-}Cp)_2ZrCl_2$	40
$(1,2,4\text{-}^tBu_3\text{-}Cp)(Cp)ZrCl_2$	54.5

[a] Values taken from paper by Janiak *et al.*[140]
[b] Brintzinger *et al.* calculated a value of 95° for this parameter.[233]

6. Conclusions

This review has focused on the Group 4 bis-cyclopentadienyl metallocenes and their role in polymerisation reactions. These catalysts however constitute only a subsection of the SCC type. There has been much activity in the search for alternative polymerisation catalysts such as the constrained geometry metallocenes and non-Group 4 metal catalysts. This work has been comprehensively covered in recent reviews (Table 4, see Appendix). Metallocene catalysts have also been successfully engaged in catalytic organic reactions, such as enantioselective C–C and C–H bond formations.[18] Organic transformations, where stereoselectivity is an issue, include asymmetric epoxidations,[234] hydrogenations,[235-237] stereoselective cyclisations,[238-241] Diels-Alder reactions,[215,242,243] alkene isomerisations[211] and cross-coupling reactions.[244]

This review has attempted to illustrate the ingenuity scientists have shown in designing tools with which to dictate how simple α-olefins can be catalytically knitted together to form useful polymeric products. By trying to understand the details of how these polymerisation reactions occur new rules for the synthesis of better catalysts have been discovered.

7. Tables of Polymerisation Data

The tables of polymerisation data (see Appendix: Tables 4 - 10) allow for a comparison of the polymerisation data generated from different catalysts in different laboratories. Although it is comprehensive, it is far from exhaustive and only the polymerisation data from the major chemistry journals have been included. Due to the enormity of this task, errors may be inevitable, but care has been taken to ensure that these have been kept to a minimum.

Abbreviations

An	anisidine (4-methoxyaniline), 4-CH_3-3,5-^{t}$Bu_2C_6H_2$
Bz	benzyl, –$CH_2(C_6H_5)$
COD	*cis, cis*-1,5-cyclooctadiene
Cp	cyclopentadienyl, η^5–C_5H_5
^{c}Pe	*cyclo*-pentyl
Cp*	pentamethylcyclopentadienyl, η^5–C_5Me_5
Cp$_{cen}$	the centroid of a cyclopentadienyl or indenyl ligand
Cy	cyclohexyl, –C_6H_{11}
DSC	Differential Scanning Calorimetry
EAO	ethylaluminoxane
ebmp	2,2'-ethylenebis(6-*tert*-butyl-4-methylphenolato)
ebthi	1,2-ethylene-1,1'-bis(η^5–tetrahydroindenyl)
Et	ethyl, –CH_2CH_3
ETE	Electron Transfer Equilibria
Flu	fluorenyl, η^5–$C_{13}H_8$
GC	Gas Chromatography
Ind	indenyl, η^5–C_9H_7
IndH$_4$	tetrahydroindenyl, η^5–C_9H_{11}
^{i}Pr	*iso*-propyl, –$CH(CH_3)_2$
l.p.	liquid propene
Me	methyl, –CH_3

MAO	methylaluminoxane
mbmp	2,2'-methylenebis(6-*tert*-butyl-4-methylphenolato)
MW	molecular weight
MS	Mass Spectrometry
Naph	Naphthyl, ($C_{10}H_7$)
n.g	not given.
PBB	*tris*-(2,2',2"-perfluorobiphenyl)borane
PE	polyethene
Ph	phenyl
PNB	*tris*-(β-perfluoronaphthyl)borane
PP	polypropene
^{c}Pr	*cyclo*-propyl
r.t.	room temperature
sibmp	2,2'-sulfinylbis(6-*tert*-butyl-4-methylphenolato)
SCC	Single Centre Catalyst
^{t}Bu	*tert*-butyl, $-C(CH_3)_3$
tbmp	2,2'-thiobis(6-*tert*-butyl-4-methylphenolato)
TBS	*tertiary*-butyldimethylsilyl, $–SiMe_2(C(CH_3)_3)$
TCP	2-(tetramethylcyclopentadienyl)-4-methylphenolate
TIBA	tri-*iso*-butylaluminium
TIPP	2, 4, 6-tri-(*iso*-propyl)phenyl
TIPS	tri-*iso*-propylsilyl, $–Si(CH(CH_3)_2)_3$
TP	hydrotris(pyrazolyl)borate
TP*	hydro-*tris*-(3,5-dimethylpyrazolyl)borate
UV	Ultra-Violet Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
Z-N	Ziegler-Natta

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Appendix

Table 4 List of recent review articles concerning Single Site Catalysts used for olefin polymerisations.[a]

Author(s)	Title	Ref.
R.F. Jordan	Chemistry of cationic dicyclopentadienyl group 4 metal-alkyl complexes	13
P.C. Möhring and N.J. Coville	Homogeneous group 4 metallocene Ziegler-Natta catalysts: the influence of cyclopentadienyl ring substituents.	14
H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R.M. Waymouth	Stereospecific olefin polymerisation with chiral metallocene catalysts.	15
W. Kaminsky and M. Arndt	Metallocenes for polymer catalysis	16
M. Bochmann	Cationic Group 4 metallocene complexes and their role in polymerisation catalysis: the chemistry of well defined Ziegler catalysts.	17
A.H. Hoveyda and J.P. Morken	Enantioselective C–C and C–H bond formation mediated or catalyzed by chiral *ebthi* complexes of Titanium and Zirconium.	18
J.A. Ewen	New chemical tools to create plastics.	19
M. Hackmann and B. Rieger	Metallocene catalysis.	20
K. Mashima, Y. Nakayama and A. Nakamura	Recent trends in the polymerization of α-olefins catalysed by organometallic complexes of early transition metals.	21
N. Tomotsu, N. Ishihara, T.H. Newman and M.T. Malanga	Syndiospecific polymerization of styrene.	22
H.G. Alt and E. Samuel	Fluorenyl complexes of zirconium and hafnium as catalysts for olefin polymerization.	23
W. Kaminsky	Highly active metallocene catalysts for olefin polymerization.	24
A.L. McKnight and R.M. Waymouth	Group 4 *ansa*-cyclopentadienyl-amido catalysts for olefin polymerization.	25
W.E. Piers	Zwitterionic metallocenes.	26
K.H. Theopold	Homogeneous chromium catalysts for olefin polymerisation.	27
P. Jutzi and T. Redeker	Aminoethyl-functionalized cyclopentadienyl complexes of d-block elements.	28
G.J.P. Britovsek, V.C. Gibson and D.F. Wass	The search for new-generation olefin polymerization catalysts: life beyond metallocenes.	29
S.D. Ittel, L. K. Johnson and M. Brookhart	Late-Metal catalysts for ethylene homo- and copolymerization.	30
H.G. Alt and A. Köppel	Effect of the nature of metallocene complexes of Group 4 metals on their performance in catalytic ethylene and propene polymerization.	31

Table 4 (cont.)

Author(s)	Title	Ref.
G.W. Coates	Precise control of polyolefin stereochemistry using single-site metal catalysts.	32
L. Resconi, L. Cavallo, A. Fait and F. Piemontesi	Selectivity in propene polymerisation with metallocene catalysts.	33
G.G. Hlatky	Heterogeneous single-site catalysts for olefin polymerization.	34
G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla and B. Tesche	Propene polymerization with silica-supported metallocene/MAO catalysts.	35
E.Y.-X. Chen and T.J. Marks	Cocatalysts for metal-catalyzed olefin polymerization: activators, activation processes, and structure-activity relationships.	36
A.K. Rappé, W.M. Skiff and C.J. Casewit	Modelling metal-catalyzed polymerization.	37
K. Angermund, G. Fink, V.R. Jensen and R. Kleinschmidt	Toward quantitative prediction of stereospecificty of metallocene-based catalysts for α-olefin polymerization.	38
M.C. Baird	Carbocationic alkene polymerizations initiated by organotransition metal complexes: an alternative, unusual role for soluble Ziegler-Natta catalysts.	39
L.S. Boffa and B.M. Novak	Copolymerization of polar monomers with olefins using transition-metal complexes.	40
U. Siemeling	Chelate complexes of cyclopentadienyl ligands bearing pendant O-donars.	41
H. Butenschön	Cyclopentadienylmetal complexes bearing pendant phosphorus, arsenic, and sulfur ligands.	42

[a] The reviews in this table are catalogued in chronological order according to date of publication.

Table 5 Ethene polymerisation reactions of Group 4 metallocene catalysts.

Metallocene	Polymerisation Conditions					Activity/	Analyses[e]	Ref.
	mol M/ $\times 10^{-6}$mol[a]	[M]/ $\times 10^{-6}$M[b]	[Al]:[M][c]	T/ °C	P/ Bar[d]	$\times 10^{5}$g PE (mol M h)$^{-1}$		
1. Metallocenes with two cyclopentadienyl-type ligands								
1.1. (Cp^1)(Cp^2)MX								
M=Ti, X=Cl_2								
Cp^1=Cp^2=Cp	2.5	50	4000	20	1	64.7	MW, DSC	245
Cp^1=Cp^2=1,2-$(CH_2)_2$Cp	8	32	5000	40	1.2	0.254	MW	87
M=Zr, X=Cl_2								
Cp^1=Cp^2=Cp	11	55	3000	80	1.6	93.00	MW, DSC	246
	3.0	10	4000	70	5	1.85	MW	139, 140
	3.0	10	4000	70	5	1.15	MW	140
	0.078	0.25	160000	70	5	37.8	MW, η	139, 140
	0.078	0.25	160000	70	5	38.7	MW, η, DSC	140
	(n.g.)	(n.g.)	6000	30	2	22.0	MW	247
	2.5	1.47	1500	80	10	75.00	MW	247
	3.4-17	6.8-34	20000	60	10	1370	MW, DSC	248
	1	5.0	1000	40	1	105	MW	249
	(n.g.)	(n.g.)	5000	60	10	1100	MW, DSC	88
	0.4	2.0	10000	40	1	236	MW	249
	0.0416	0.104	30000	50	2	668	MW, DSC	229
Cp^1=Cp^2=CpMe	0.0416	0.104	30000	50	2	754	MW, DSC	229
Cp^1=Cp^2=CpEt	0.0416	0.104	30000	50	2	972	MW, DSC	229
Cp^1=Cp^2=Cp^{i}Pr	0.0416	0.104	30000	50	2	870	MW, DSC	229
Cp^1=Cp^2=Cp^{t}Bu	0.0416	0.104	30000	50	2	206	MW, DSC	229
Cp^1=Cp^2=CpSiMe$_3$	0.0416	0.104	30000	50	2	923	MW, DSC	229
Cp^1=Cp^2=CpCMe$_2$Ph	0.0416	0.104	30000	50	2	19.2	MW, DSC	229
Cp^1=Cp, Cp^2= Me$_4$Cp	3.0	10	4000	70	5	1.5	MW	139, 140
	0.078	0.25	160000	70	5	23.1	MW, η, DSC	139, 140
Cp^1=Cp^2=Me$_4$Cp	3.0	10	4000	70	5	1.5	MW	139, 140
	0.078	0.25	160000	70	5	8.25	MW, η	139, 140
Cp^1=Cp, Cp^2= PC$_4$Me	3.0	10	4000	70	5	1.85	MW	139, 140
	0.078	0.25	160000	70	5	13.1	MW, η	139, 140
Cp^1=Cp^2= PC$_4$Me$_4$	3.0	10	4000	70	5	0.55	MW	139, 140
	0.078	0.25	160000	70	5	0.70	MW, η	139, 140
Cp^1=Cp, Cp^2=Cp*	3.0	10	4000	70	5	1.5	MW	139, 140
	0.078	0.25	160000	70	5	18.6	MW, η, DSC	139, 140
Cp^1=Cp^2= Cp*	3.0	10	4000	70	5	0.95	MW	139, 140
	0.078	0.25	160000	70	5	1.75	MW, η	139, 140
Cp^1=Cp, Cp^2= ^{t}BuCp	3.0	10	4000	70	5	1.1	MW	140
	0.078	0.25	160000	70	5	13.9	DSC	140
CpR^1=CpR^2=^{t}BuCp	3.0	10	4000	70	5	0.45	MW	140
	0.078	0.25	160000	70	5	0.75	DSC	140
Cp^1=Cp^2=1,3-^{t}Bu$_2$Cp	3.0	10	4000	70	5	0.65	MW	140
	0.078	0.25	160000	70	5	1.35	DSC	140
Cp^1=Cp^2= 1,3-^{t}Bu$_2$Cp	3.0	10	4000	70	5	0.01		140
Cp^1=Cp, Cp^2=1,3,4-^{t}Bu$_3$Cp	3.0	10	4000	70	5	0.65	MW	140
	0.078	0.25	160000	70	5	0.35	DSC	140
Cp^1=Cp^2=1,2-$(CH_2)_2$Cp	1.2	4.8	5000	40	1.2	78.96	MW	87
Cp^1=Cp^2=(1,3-Me$_2$-2-Ph)Cp	0.5	2.5	5800	80	2.75	328	MW	250
Cp^1=Cp^2=(1,3-Me$_2$-2-^{n}Bu)Cp	0.5	2.5	5800	80	2.75	480	MW	250
Cp^1=Cp^2=(1,3-Me$_2$-2-^{t}Bu)Cp	0.5	2.5	5800	80	2.75	152	MW	250

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.^{e}	Ref.
	mol M/ $\times10^{-6}$mol ^{a}	[M]/ $\times10^{-6}$M ^{b}	[Al]:[M] ^{c}	T/ ^{o}C	P/ Bar ^{d}	$\times10^5$g PE (mol M h)$^{-1}$		
Cp^1=Cp^2=(1,3-Me$_2$-2-(CH$_2$)$_4$-OMe)Cp	0.5	2.5	5800	80	2.75	120	MW	250
Cp^1=Cp^2=(1,3,3,5,5-pentamethyl-cyclohexyl)Cp	6.25	2.98	(n.g.)	30	2	3.2		251
Cp^1=Cp, Cp^2=Cp(C$_2$H$_2$NMe$_2$)	2.5	50	4000	20	1	52.9	MW, DSC	245
Cp^1=Cp^2=Cp[(CH)$_2$O(CH$_2$)$_2$OCH$_2$CH$_3$]	0.5	2.5	5000	80	2.8	trace	MW	252
Cp^1=Cp^2=Cp[(CH)$_4$O(CH$_2$)$_2$OCH$_2$CH$_3$]	0.5	2.5	5000	80	2.8	92.0	MW	252
Cp^1=Cp^2=Cp[(CH)$_6$O(CH$_2$)$_2$OCH$_2$CH$_3$]	0.5	2.5	5000	80	2.8	316	MW	252
Cp^1=Cp^2=Cp[(CH)$_8$O(CH$_2$)$_2$OCH$_2$CH$_3$]	0.5	2.5	5000	80	2.8	120	MW	252
Cp^1=Cp^2=Cp[(CH$_2$)$_2$OCH$_2$CH$_3$]	0.5	2.5	5000	80	2.8	25.6	MW	252
Cp^1=Cp^2=CpSi[(Me)$_2$(NH^{n}Bu)]	(n.g.)	(n.g.)	5000	60	10	680	MW, DSC	88
M=Zr, X=Phenoxy and/or Cl								
Cp^1=Cp^2=Cp, X=Cl + 2,6-di-^{t}Bu-phenol	(n.g.)	(n.g.)	6000	30	2	4.00	MW	247
	5.0	17	1500	80	10	97.00	MW	247
Cp^1=Cp^2=Cp, X=Cl + 2,6-di-^{i}Pr-phenol	(n.g.)	(n.g.)	6000	30	2	19.10	MW	247
Cp^1=Cp^2=Cp, X= (2,6-dimethyl-phenol)$_2$	(n.g.)	(n.g.)	6000	30	2	17.40	MW	247
M=Zr, X=Me$_3$SiNCH$_2$CH$_2$NSiMe$_3$								
Cp^1=Cp^2=Cp	3540	39333	1000	25	1	22.8		253
	3540	39333	2000	25	1	75.3		253
	3540	39333	3000	25	1	65.2		253
	3540	39333	1000	60	1	27.1		253
	3540	39333	2000	60	1	32.0		253
M=Hf, X=Cl$_2$								
Cp^1=Cp^2=1,2-(CH$_2$)$_2$Cp	4.8	19.2	5000	40	1.2	4.56	MW	87
1.2. B(Cp^1)(Cp^2)MCl$_2$								
M=Ti, B=SiMe$_2$								
Cp^1=Cp, Cp^2=3-(SiMe$_3$)Cp	6.25	12.5	290	30	2	16.26	MW, DSC	254
	5	10.0	290	30	10	67.10	MW, DSC	254
	5	10.0	5000	30	10	63.50	MW, DSC	254
Cp^1=Cp^2=3-(SiMe$_3$)Cp (*meso*)	5	10.0	290	30	10	8.50	MW, DSC	254
	5	10.0	290	40	10	7.93	MW, DSC	254
M=Ti, B=-Me$_2$Si-SiMe$_2$								
Cp^1=Cp^2=^{t}BuCp	0.30	3.0	2500	30	1	20.9	MW	255
M=Ti, B=-SiMe$_2$N(^{n}Bu)NMe$_2$Si-								
Cp^1=Cp^2=Cp	2.3	4.6	5000	60	10	450	MW, DSC	88
M=Zr, B=SiMe$_2$								
Cp^1=Cp, Cp^2=3-(SiMe$_3$)Cp	6.25	12.5	290	30	2	41.98	MW, DSC	254
	5	10.0	290	30	10	217.95	MW, DSC	254
	5	10.0	580	30	10	254.02	MW, DSC	254
Cp^1=Cp^2=3-(SiMe$_3$)Cp (*rac*)	6.25	12.5	290	30	2	29.26	MW, DSC	254
	5	10.0	290	30	10	51.80	MW, DSC	254
	5	10.0	290	40	10	144.34	MW, DSC	254
Cp^1=Cp, Cp^2=3-[N(^{i}Pr)$_2$]Cp	10	50	1000	30	5	0.80	MW, η	256
	10	50	1000	45	5	1.50	MW, η	256
	10	50	1000	50	5	2.50	MW, η	256
	10	50	1000	60	5	4.45	MW, η	256
	10	50	1000	90	5	9.85	MW, η	256

Table 5 (cont.)

	Polymerisation Conditions					Activity/		
Metallocene	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[M] [c]	T/ °C	P/ Bar [d]	$\times10^{5}$g PE $(\text{mol M h})^{-1}$	Anal. [e]	Ref.
M=Zr, B=-Me_2Si-$SiMe_2$								
Cp^1=Cp^2=^{t}BuCp	0.30	3.0	2500	40	1	17.9	MW	255
	0.30	3.0	2500	60	1	14.0		255
M=Zr, B= -$SiMe_2N(^nBu)NMe_2Si$-								
Cp^1=Cp^2=Cp	2.1	4.2	5000	60	10	2150	MW, DSC	88
M=Hf, B=$SiMe_2$								
Cp^1=Cp, Cp^2=3-$(SiMe_3)$Cp	6.25	12.5	290	30	2	0	MW, DSC	254
	5	10.0	290	30	10	10.34	MW, DSC	254
M=Hf, B= -$SiMe_2N(^nBu)NMe_2Si$-								
Cp^1=Cp^2=Cp	1.8	3.5	5000	60	10	140	MW, DSC	88
B=$SnMe_2$, X=NMe_2								
Cp^1=Cp^2=Cp	4.4	(n.g.)	600	70	7	68.4		
1.3. Catalysts with Intramolecular Anion-Metallocene Interactions								
$Cp^*[\eta^5,\eta^1\text{-}C_5Me_4CH_2B(C_6F_5)_2(\mu\text{-}H)]ZrCl$	20.2	202	5	25	1	0.00022	MW	257
$Cp^*[\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3]ZrCl$	16.5	165	5	25	1	0.1	MW	257
$Cp^*[\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3]ZrC_6F_5$	21.6	216	5	25	1	0.067	MW	257
1.4. $(Ind^1)(Ind^2)MCl_2$								
M=Zr								
Ind^1=Ind^2=Ind	0.15	0.5	5000	50	2.0	625.00	MW, DSC	258
	0.075	0.187	30000	50	2	587	MW, DSC	229
Ind^1=Ind^2=1-MeInd	0.075	0.187	30000	50	2	234	MW, DSC	229
Ind^1=Ind^2=2-MeInd	0.075	0.187	30000	50	2	117	MW, DSC	229
Ind^1=Ind^2=1-EtInd	0.075	0.187	30000	50	2	213	MW, DSC	229
Ind^1=Ind^2=2-EtInd	0.075	0.187	30000	50	2	64	MW, DSC	229
Ind^1=Ind^2=1-^{i}PrInd	0.075	0.187	30000	50	2	50	MW, DSC	229
	0.75	1.87	3 000	50	2	28.4	MW, DSC	229
Ind^1=Ind^2=2-^{i}PrInd	(n.g.)	(n.g.)	3500	0	1	21	MW	259
Ind^1=Ind^2=2-^{n}BuInd	(n.g.)	(n.g.)	3500	0	1	6.0	MW	259
Ind^1=Ind^2=1-^{t}BuInd	0.75	1.87	3 000	50	2	3.2	MW, DSC	229
Ind^1=Ind^2=1-$SiMe_3$-Ind	0.075	0.187	30000	50	2	60	MW, DSC	229
	0.75	1.87	3 000	50	2	41.6	MW, DSC	229
Ind^1=Ind^2=2-$SiMe_3$-Ind	0.75	1.87	3 000	50	2	3.7	MW, DSC	229
Ind^1=Ind^2=2-CyInd	(n.g.)	(n.g.)	3500	0	1	25	MW	259
Ind^1=Ind^2=1-BzInd (100% *rac*)	0.075	0.187	30000	50	2	57	MW, DSC	229
	0.75	1.87	3 000	50	2	31.0	MW, DSC	229
Ind^1=Ind^2=1-BzInd (100% *meso*)	0.075	0.187	30000	50	2	40	MW, DSC	229
	0.75	1.87	3 000	50	2	29.7	MW, DSC	229
Ind^1=Ind^2=2-BzInd	(n.g.)	(n.g.)	3500	0	1	19	MW	259
	0.075	0.187	30000	50	2	39	MW, DSC	229
	0.75	1.87	3 000	50	2	11.9	MW, DSC	229
Ind^1=Ind^2=1-PhInd	0.075	0.187	30000	50	2	264	MW, DSC	229
	0.75	1.87	3 000	50	2	108	MW, DSC	229
Ind^1=Ind^2= 2-PhInd	0.5		2750	20	1.7	35.70	MW	126
	0.075	0.187	30000	50	2	43	MW, DSC	229
	0.75	1.87	3 000	50	2	23.8	MW, DSC	229
Ind^1=Ind^2=1-(1)-Naph-Ind	0.75	1.87	3 000	50	2	traces		229
Ind^1=Ind^2= *meso*-1-Me-2-PhInd	0.5		2750	20	1.7	30.50	MW	126
Ind^1=Ind^2= *rac*-1-Me-2-PhInd	0.5		2750	20	1.7	72.80	MW	126
Ind^1=Ind^2=(*p*-FPh)Ind	0.6	2	5000	50	2.0	68.24	MW, DSC	258
Ind^1=Ind^2=[4,7-Me_2-2-$OSi(Me)_2(^tBu)$]Ind	11	55	3000	80	1.6	5.00	MW, DSC	246
	11	55	500	80	1.6	2.50	MW, DSC	246

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.^{e}	Ref.
	mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[M]^{c}	T/ °C	P/ Bar ^{d}	$\times 10^{5}$g PE (mol M h)$^{-1}$		
Ind^{1}=Ind^{2}=[2-OSi(Me)$_2$(^{t}Bu)]cyclopenta [*l*]-phenanthryl	11	55	3000	80	1.6	17.00	MW, DSC	246
	11	55	500	80	1.6	5.00	MW, DSC	246
M=Hf								
Ind^{1}=Ind^{2}=Ind	1.5	5	5000	50	2.0	78.12	MW, DSC	258
Ind^{1}=Ind^{2}=(*p*-FPh)Ind	1.5	5	5000	50	2.0	26.45	MW, DSC	258
1.5. (Cp)(Ind)MCl$_2$								
M=Zr								
Cp=Cp, Ind=1-BzInd	2.3	4.6	17000	60	10	1600	MW, DSC, XRD	260
1.6. B(Ind^{1})(Ind^{2})MX								
M=Zr, X=Cl$_2$, B=CR^{1}CR^{2}								
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=Ind	0.6	2	5000	50	2.0	93.77	MW, DSC	258
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=(*p*-FPh)Ind	3	10	5000	50	2.0	14.73	MW, DSC	258
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=2-OSi(Me)$_2$(^{t}Bu)Ind	3	15.0	3000	20	2.5	29	MW, DSC	261
	3	15.0	3000	40	2.5	18	MW, DSC	261
	3	15.0	3000	60	2.5	27	MW, DSC	261
	3	15.0	3000	80	2.5	59	MW, DSC	261
	3	15.0	100	40	2.5	27	MW, DSC	261
	3	15.0	250	40	2.5	23	MW, DSC	261
	3	15.0	500	40	2.5	23	MW, DSC	261
	3	15.0	10000	40	2.5	21	MW, DSC	261
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=2-OSi(Me)$_2$(^{t}Bu)IndH$_4$	3	15.0	3000	20	2.5	9.0	MW, DSC	261
	3	15.0	3000	40	2.5	37	MW, DSC	261
	3	15.0	3000	60	2.5	37	MW, DSC	261
	3	15.0	100	40	2.5	7.0	MW, DSC	261
	3	15.0	250	40	2.5	11	MW, DSC	261
	3	15.0	500	40	2.5	33	MW, DSC	261
	3	15.0	10000	40	2.5	25	MW, DSC	261
M=Hf, X=Cl$_2$, B=CR^{1}CR^{2}								
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=Ind	1.5	5	5000	50	2.0	21.01	MW, DSC	258
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=(*p*-FPh)Ind	3	10	5000	50	2.0	1.53	MW, DSC	258
CR^{1}CR^{2}=C$_2$H$_4$, Ind^{1}=Ind^{2}=2-OSi(Me)$_2$(^{t}Bu)Ind	3	15.0	3000	20	2.5	0	MW, DSC	261
	3	15.0	3000	40	2.5	5.0	MW, DSC	261
	3	15.0	3000	60	2.5	21	MW, DSC	261
	3	15.0	3000	80	2.5	34	MW, DSC	261
	3	15.0	100	40	2.5	5.0	MW, DSC	261
	3	15.0	250	40	2.5	13	MW, DSC	261
	3	15.0	500	40	2.5	10	MW, DSC	261
	3	15.0	10000	40	2.5	2.0	MW, DSC	261
M=Zr, X=Cl$_2$, B=SiMe$_2$								
Ind^{1}=Ind^{2}=Ind	0.25	0.3	15000	70	5	1080	MW	94
Ind^{1}=Ind^{2}=2-MeInd	0.25	0.3	15000	70	5	1260	MW	94
Ind^{1}=Ind^{2}=2-PhInd (100% rac)	0.5	5	1000	(n.g.)	2.1	32.70	MW	131
(100% meso)	0.5	5	1000	(n.g.)	2.1	26.10	MW	131
Ind^{1}=Ind^{2}=4-PhInd	0.25	0.3	15000	70	5	580	MW	94
Ind^{1}=Ind^{2}=2-Me-4-^{i}PrInd	0.25	0.3	15000	70	5	3290	MW	94
Ind^{1}=Ind^{2}=2-Me-4-PhInd	0.25	0.3	15000	70	5	9220	MW	94
Ind^{1}=Ind^{2}=2-Me-5-PhInd	0.25	0.3	15000	70	5	750	MW	94

Table 5 (cont.)

Metallocene	Polymerisation Conditions mol M/ $\times 10^{-6}$mol [a]	[M]/ $\times 10^{-6}$M [b]	[Al]:[M] [c]	T/ °C	P/ Bar [d]	Activity/ $\times 10^5$g PE (mol M h)$^{-1}$	Anal. [e]	Ref.
$Ind^1=Ind^2$=2-Me-4-(1-Naph)Ind	0.25	0.3	1500	70	5	5100	MW	94
$(Ind^1)=(Ind^2)$= benz[*e*]indenyl	0.25	0.3	15000	70	5	5120	MW	94
$(Ind^1)=(Ind^2)$= 2-methylbenz[*e*]indenyl	0.25	0.3	15000	70	5	6170	MW	94
M=Zr, X=Cl_2, B=$SiPh_2$								
$Ind^1=Ind^2$=Ind	(n.g.)	1.0	1000	40	1	35	NMR, MW, DSC	262
	(n.g.)	1.0	1000	60	1	80	NMR, MW, DSC	262
M=Zr								
B= -$SiMe_2$-O-Me_2Si-, $Ind^1=Ind^2$=Ind	2.5	50	4000	-20	1	17.5	MW, DSC	263
	2.5	50	4000	20	1	16.3	MW, DSC	263
B= -$SiMe_2N(^nBu)NMe_2Si$-, $Ind^1=Ind^2$=Ind	1.81	3.6	5000	60	10	1400	MW, DSC	88
M=Hf								
B= -$SiMe_2$-O-Me_2Si-, $Ind^1=Ind^2$=Ind	2.5	50	4000	-20	1	2.4	MW, DSC	263
	2.5	50	4000	0	1	27.1	MW, DSC	263
	2.5	50	4000	20	1	32.6	MW, DSC	263
1.7. B(Cp)(Ind)MCl_2								
M=Zr								
B= -CMe_2, Cp=Cp, Ind=3-BzInd	2.1	4.2	17000	60	10	130	MW, DSC, XRD	260
B= -$SiMe_2$ Cp=Cp, Ind=3-BzInd	2.0	4.1	17000	60	10	814	MW, DSC, XRD	260
M=Hf								
B= -CMe_2, Cp=Cp, Ind=3-BzInd	1.8	3.5	17000	60	10	4.5	MW, DSC,XRD	260
1.8. (Flu)(Cp)MCl_2								
M=Zr								
Flu=Flu, Cp=Cp	5.09	10.1	(n.g.)	30	10	16.1		264
Flu=2,7-Br_2Flu, Cp=Cp	2.73	5.46	(n.g.)	30	10	5.5		264
Flu=2,7-Me_2Flu, Cp=Cp	3.56	7.12	(n.g.)	30	10	21.3		264
Flu=2,7-$^tBu_2$Flu, Cp=Cp	2.97	5.94	(n.g.)	30	10	21.9		264
Flu=2,7-$(OMe)_2$Flu, Cp=Cp	4.19	8.39	(n.g.)	30	10	4.0		264
Flu=9-MeFlu, Cp=Cp	4.9	9.8	(n.g.)	30	10	0.231		265
Flu=9-^{i}PrFlu, Cp=Cp	3.5	6.9	(n.g.)	30	10	0.340		265
Flu=9-^{t}BuFlu, Cp=Cp	4.0	8.0	(n.g.)	30	10	0.386		265
Flu=9-$SiMe_3$Flu, Cp=Cp	1.9	3.9	(n.g.)	30	10	0.336		265
Flu=9-CyFlu, Cp=Cp	3.2	6.3	(n.g.)	30	10	0.260		265
Flu=9-PhFlu, Cp=Cp	3.6	7.3	(n.g.)	30	10	0.165		265
Flu=9-o-TolFlu, Cp=Cp	3.5	7.0	(n.g.)	30	10	0.173		265
Flu=9-*p*-TolFlu, Cp=Cp	3.3	6.6	(n.g.)	30	10	0.181		265
Flu=9-*p*-F-C_6H_4, Cp=Cp	3.5	7.0	(n.g.)	30	10	0.083		265
Flu=Flu, Cp=Cp^*	4.5	9.1	(n.g.)	30	10	0.125		266
Flu=2,7-Me_2Flu, Cp=Cp^*	3.1	6.1	(n.g.)	30	10	0.173		266
Flu=2,7-$^tBu_2$Flu, Cp=Cp^*	3.0	5.9	(n.g.)	30	10	0.190		266
Flu=4,7-Me_2Flu, Cp=Cp^*	5.1	10	(n.g.)	30	10	0.080		266
Flu=2-^{t}BuFlu, Cp=Cp^*	3.7	7.3	(n.g.)	30	10	0.160		266
M=Hf								
Flu=Flu, Cp=Cp^*	4.4	8.7	(n.g.)	30	10	0.080		266
Flu=2,7-Me_2Flu, Cp=Cp^*	3.5	6.9	(n.g.)	30	10	0.040		266
Flu=2,7-$^tBu_2$Flu, Cp=Cp^*	3.6	7.3	(n.g.)	30	10	0.610		266

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.[e]	Ref.
	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[M][c]	T/ °C	P/ Bar [d]	$\times10^5$g PE (mol M h)$^{-1}$		
1.9. (Tp)(Cp)MCl$_2$								
M=Zr								
Tp=Tp, Cp=Cp	10	50	100	40	1	7.50	MW	249
	10	50	1000	40	1	8.08	MW	249
1.10. B(Ind)(Flu)MCl$_2$								
M=Zr, B=$Y^1R^1Y^2R^2$								
Ind=Ind, Flu=Flu								
$Y^1R^1=CH_2$, $Y^2R^2=CH[(CH_2)_2CHCH_2)]$	1.9	3.83	17 000	60	10	115.00	MW, DSC	267
$Y^1R^1=CH_2$, $Y^2R^2=CH[(CH_2)_3CHCH_2)]$	1.8	3.64	17 000	60	10	93.00	MW, DSC	267
$Y^1R^1=CH_2$, $Y^2R^2=CH[(CH_2)_5CHCH_2)]$	1.7	3.46	17 000	60	10	173.00	MW, DSC	267
$Y^1R^1=Y^2R^2=CH_2CH_2$								
Ind=Ind, Flu=Flu	0.25	5	4000	50	1	40		268
Ind=2-MeInd, Flu=Flu	0.25	5	4000	50	1	266		268
Ind=4,7-Me$_2$Ind, Flu=Flu	0.25	5	4000	50	1	172		268
Ind=2,4,7-Me$_3$Ind, Flu=Flu	0.25	5	4000	50	1	264		268
Ind=3-[CH$_2$CHCH$_2$]Ind, Flu=Flu	1.9	3.95	17 000	60	10	1530.00	MW, DSC	267
Ind=3-[(CH$_2$)$_2$CHCH$_2$)]Ind, Flu=Flu	1.9	3.83	17 000	60	10	1980.00	MW, DSC	267
Ind=3-[(CH$_2$)$_3$CHCH$_2$)]Ind, Flu=Flu	1.9	3.73	17 000	60	10	2040.00	MW, DSC	267
Ind=3-[(CH$_2$)$_4$CHCH$_2$)]Ind, Flu=Flu	1.8	3.63	17 000	60	10	1980.00	MW, DSC	267
Ind=3-[SiMe$_2$(CH$_2$)$_4$CHCH$_2$)]Ind, Flu=Flu	1.6	3.28	17 000	60	10	608.00	MW, DSC	267
Ind=3-(CH$_2$Ph)Ind, Flu=Flu	1.8	3.58	17 000	60	10	1100.00	MW, DSC	267
1.11. B(Flu^1)(Flu^2) MCl$_2$								
M=Zr, B=YR^1R^2								
$YR^1R^2=CH(^nC_4H_9)$, Flu^1=Flu^2=Flu	22.47	11.24	5000	90	30	39.50		269
$YR^1R^2=Si(Me)(CH_2CHCH_3)$	1.7-3.5	3.4-6.8	2500	20	10	580.00	MW, DSC	270
M=Zr, B=$Y^1R^1Y^2R^2$								
Flu^1=Flu, Flu^2=2,7-[(CH$_2$)$_6$CHCH$_2$]								
$Y^1R^1=Y^2R^2=CH_2CH_2$	1.4-2.7	2.7-5.3	2500	20	10	563.00	MW, DSC	270
Flu^1=Flu^2=Flu								
$Y^1R^1=Y^2R^2=CH_2CH_2$	0.98	0.49	500	100	14	49261	MW	271
$Y^1R^1=Y^2R^2=CH(^nC_4H_9)$	22.19	11.10	5000	90	30	89.60		269
$Y^1R^1=CH_2$, $Y^2R^2=[CH(CH_2)_4CHCH_2]$	1.6	3.33	17 000	60	10	3330.0	MW, DSC	267
$Y^1R^1=CH_2$, $Y^2R^2=[CH(CH_2)_6CHCH_2]$	1.6	3.18	17 000	60	10	2900.0	MW, DSC	267
$Y^1R^1=SiMe_2$, $YR^2=CH_2$	1.8-8.9	3.6-18	20000	60	10	1240	MW, DSC	248
$Y^1R^1=Y^2R^2=SiMe_2$	1.7-8.2	3.3-17	20000	60	10	96	MW, DSC	248
M=Hf, B=YR^1R^2								
$YR^1R^2=CH(^nC_4H_9)$, Flu^1=Flu^2=Flu	23.46	11.73	5000	90	30	0.30		269
M=Hf, B=$Y^1R^1Y^2R^2$								
Flu^1=Flu^2=Flu								
$Y^1R^1=Y^2R^2=CH_2CH_2$	0.98	0.49	500	100	14	2677	MW	271
$Y^1R^1=Y^2R^2=CH(^nC_4H_9)$	22.03	11.02	5000	90	30	11.40		269
$Y^1R^1=CH_2$, $Y^2R^2=(CH(CH_2)_4CHCH_2)$	1.5	2.91	17 000	60	10	30.00	MW, DSC	267
$Y^1R^1=SiMe_2$, $Y^2R^2=CH_2$	1.5-7.7	3.1-1.5	20000	60	10	72	MW, DSC	248

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.[e]	Ref.
	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[M][c]	T/ °C	P/ Bar [d]	$\times10^5$g PE (mol M h)$^{-1}$		
1.12. B(Cp)(Flu)MCl$_2$								
M=Zr,B=YR^{1}R^2								
YR^{1}R^2=C(Me)((CH$_2$)$_2$CHCH$_3$), Cp=Cp, Flu=Flu	2.1-4.2	4.1-8.3	5000	20	10	79.00	MW, DSC	270
B=SiMe$_2$, Cp=Cp, Flu=Flu	0.5	10	7000	0	1	10.3	MW, DSC	272
	0.5	10	6000	50	1	43.2	MW, DSC	272
1.13. B(Ind)(Flu)MCl$_2$								
M=Zr, B=SiMe$_2$								
Ind=Ind, Flu=Flu	0.5	10	6000	50	1	1.08	MW, DSC	272
2. Metallocenes with one cyclopentadienyl-type ligand								
2.1. (Cp)(NPR$_3$)TiL								
L=Cl$_2$								
Cp=Cp, R=Cy	38.5	(n.g.)	500	25	1	0.42	MW	273
Cp=Cp, R=^{i}Pr	26.5	(n.g.)	500	25	1	0.49	MW	273
Cp=Cp, R=^{t}Bu	31.0	(n.g.)	500	25	1	5.00	MW	273
Cp=^{t}BuCp, R=Cy	25.8	(n.g.)	500	25	1	0.46	MW	273
Cp=^{t}BuCp, R=^{i}Pr	37.2	(n.g.)	500	25	1	0.16	MW	273
Cp=^{t}BuCp, R=^{t}Bu	21.9	(n.g.)	500	25	1	8.81	MW	273
2.2. (Cp)ML								
M=Ti, L=Cl$_3$								
Cp=Cp	2.5	50	4000	20	1	0.228	MW, DSC	245
	5	25	1000	40	1	0.13		249
	40	1000	400	50	1	0.117	MW, DSC	274
(+2eq. NHEt$_2$)	40	1000	400	50	1	0.077	MW, DSC	274
Cp=Cp*	2.5	50	4000	20	1	2.10	MW, DSC	245
	40	1000	400	50	1	0.030	MW, DSC	274
(+2eq. NHEt$_2$)	40	1000	400	50	1	0.0063	MW, DSC	274
Cp=(Me)$_4$(CH$_2$CH$_2$Ph)Cp	2.5	50	2000	20	1	7.87	MW, DSC	275
	2.5	50	4000	20	1	13.9	MW, DSC	275
	2.5	50	4000	50	1	7.05	MW, DSC	275
M=Zr, L=Cl$_3$								
Cp=Cp	10	50	100	40	1	0.45	MW	249
	10	50	1000	40	1	0.26	MW	249
	40	1000	100	50	1	0.198	MW, DSC	274
	40	1000	400	50	1	0.159	MW, DSC	274
	40	1000	1000	50	1	0.140	MW, DSC	274
	40	1000	3[f]	50	1	0.0503	MW, DSC	274
	40	1000	10[f]	50	1	0.307	MW, DSC	274
	40	1000	40[f]	50	1	0.359	MW, DSC	274
M=Zr								
Cp=Cp, L=Cl$_2$ + -N(SiMe$_3$)CH$_2$CH$_2$OMe	2.7	5.4	5000	60	10	39	MW, DSC	276
Cp=Cp, L=Cl$_2$ + -N(SiMe$_3$)CH$_2$CH$_2$NMe$_2$	2.6	5.2	5000	60	10	21	MW, DSC	276
(η^5:η^1-CpR)ML								
M=Ti								
Cp=Cp, R=(CH$_2$)$_2$Ph (*i.e.* no η^1), L=Cl$_3$	2.5	50	4000	20	(n.g.)	0.155		277
	0.05	1	20000	20	(n.g.)	1.32		277
	0.05	1	20000	50	(n.g.)	3.70		277
Cp=Cp, R=C$_2$H$_4$NMe$_2$, L=Cl$_3$	2.5	50	4000	20	1	17.8	MW, DSC	245
Cp=Cp, R=CH$_2$-2-C$_5$H$_4$N, L=Cl$_3$	2.5	50	2000	75	(n.g.)	3.02	MW	277
Cp=Cp, R=SiMe$_2$N(^{t}Bu), L=Cl$_2$	(n.g.)	(n.g.)	1000	60	10	4.50	MW, DSC	278
Cp=CpMe$_4$, R=C$_2$H$_4$NMe$_2$, L=Cl$_3$	2.5	50	4000	20	1	0.72	MW, DSC	245

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.[e]	Ref.
	mol M/ ×10^{-6}mol[a]	[M]/ ×10^{-6}M[b]	[Al]:[M][c]	T/ °C	P/ Bar[d]	×10^5g PE (mol M h)$^{-1}$		
Cp=CpMe$_4$, R=(CH$_2$)$_2$Ph (*i.e.* no η^1), L=Cl$_3$	2.5	50	4000	20	(n.g.)	14.5		277
	2.5	50	4000	50	(n.g.)	7.35		277
Cp=CpMe$_4$, R=SiMe$_2$N(^{t}Bu), L=Cl$_2$	5	(n.g.)	500	23	3	9.50	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(^{i}Pr), L=Cl$_2$	5	(n.g.)	500	23	3	1.00	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(Bz), L=Cl$_2$	5	(n.g.)	500	23	3	30.90	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(1-adamantyl), L=Cl$_2$	5	(n.g.)	500	23	3	4.60	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(Bz), L=Cl + C$_6$H$_4$(CH$_2$NMe$_2$-2)	5	(n.g.)	500	23	3	20.60	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(Bz), L=Cl + [Cp(CH$_2$NMe$_2$-2)]Fe(Cp)	5	(n.g.)	500	23	3	0.80	DSC	279
Cp=CpMe$_4$, R=SiMe$_2$N(CH$_2$CH$_2$SMe), L=Bz$_2$	5	25	500	25	3	1.14	DSC	280
M=Ti, L=[N(Et)$_2$]$_2$ + NEt$_2$H								
Cp=CpMe$_4$, R=SiMe$_2$NCH$_2$CH$_2$Si(OCH$_3$)$_3$	(n.g.)	(n.g.)	800	20	1	0.193	MW, DSC	281
M=Zr, L=Cl$_2$								
Cp=Cp, R=(CH$_2$)$_3$NMe	9.9	33	520	80	20	16.7		282
	42	210	520	80	20	23.67		282
Cp=Cp, R=(CH$_2$)$_2$N(^{i}Pr)	40	200	520	50	5	0.60		282
	40	200	520	80	20	1.70		282
	9.9	33	520	80	20	0.81		282
Cp=Cp, R=(CH$_2$)$_3$N(^{i}Pr)	40	200	520	50	5	0.65		282
	42	210	520	80	20	8.29		282
	9.9	33	520	80	20	6.06		282
Cp=Cp, R=(CH$_2$)$_2$N(^{t}Bu)	44	220	520	80	20	1.55		282
Cp=Cp, R=SiMe$_2$N(^{t}Bu)	(n.g.)	(n.g.)	1000	60	10	1.1	MW, DSC	278
Cp=CpMe$_4$, R=SiMe$_2$N(^{t}Bu)	60	200	520	80	20	27.50		282
	9.9	33	520	80	20	6.67		282
	(n.g.)	(n.g.)	1000	60	10	12.90	MW, DSC	278
Cp=CpMe$_4$, R=SiMe$_2$N(CH$_2$CH$_2$OMe)	2.8	5.6	5000	60	10	43	MW, DSC	276
Cp=CpMe$_4$, R=SiMe$_2$N(CH$_2$CH$_2$NMe$_2$)	2.7	5.4	5000	60	10	29	MW, DSC	276
Cp=Cp^{t}Bu, R=SiMe$_2$N(^{t}Bu)	(n.g.)	(n.g.)	1000	60	10	1.40	MW, DSC	278
Cp=CpMe$_4$, R=SiMe$_2$N(CH$_2$CH$_2$SMe), L=Bz$_2$	5	25	500	25	3	0.15	DSC	280
M=Hf, L=Cl$_2$								
Cp=Cp, R=SiMe$_2$N(^{t}Bu)	(n.g.)	(n.g.)	1000	60	10	0.10	MW, DSC	278
M=Ti, L=(O-^{i}Pr)$_3$								
Cp=Cp, R=(CH$_2$)$_2$NMe$_2$	2.5	50	2000	50	(n.g.)	5.28	MW	277
Cp=Cp, R=(CH$_2$)$_2$N(^{i}Pr)$_2$	2.5	50	2000	50	(n.g.)	3.56	MW	277
2.4. (η^5: η^1-1-IndR)ML								
M=Ti								
Ind=Ind, R=(CH$_2$)$_2$NMe$_2$, L=Cl$_3$	2.5	50	2000	21	(n.g.)	33.8	MW, DSC	277
Ind=Ind, R=SiMe$_2$N(^{t}Bu), L=Cl$_2$	(n.g.)	(n.g.)	1000	60	10	26.00	MW, DSC	278
M=Zr, L=Cl$_2$								
Ind=Ind, R=SiMe$_2$N(^{t}Bu)	(n.g.)	(n.g.)	1000	60	10	22.70	MW, DSC	278
M=Ti, L=(O-^{i}Pr)$_3$								
Ind=Ind, R=(CH$_2$)$_2$NMe$_2$	2.5	50	2000	22	(n.g.)	15.8	MW, DSC	277
Ind=Ind, R=(CH$_2$)$_2$N(^{i}Pr)$_2$	2.5	50	2000	21	(n.g.)	0.82	MW, DSC	277
Ind=Ind, R=(CH$_2$)$_2$-2-C$_5$H$_4$N	2.5	50	2000	21	(n.g.)	0.21	MW, DSC	277

Table 5 (cont.)

	Polymerisation Conditions					Activity/		
Metallocene	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[M][c]	T/ °C	P/ Bar [d]	$\times10^5$g PE (mol M h)$^{-1}$	Anal.[e]	Ref.
2.5. (η^5: η^1-9-IndR^1)ML								
M=Zr, L=Cl_2								
Ind=Ind, R^1= -$SiMe_2N(CH_2CH_2OMe)$	2.2	4.4	5000	60	10	125	MW, DSC	276
2.6. (η^5: η^1-9-FluR^1)ML								
M=Zr, L=Cl_2								
Flu=Flu, R=$SiMe_2N(^tBu)$	(n.g.)	(n.g.)	1000	60	10	0.90	MW, DSC	278
Flu=Flu, R^1= -$SiMe_2N(CH_2CH_2OMe)$	2.2	4.4	5000	60	10	1.0	MW, DSC	276
2.7. $(C_2B_9)H_{11}ML^1L^2$								
M=Ti								
L^1=$(NEt_2)_2$, L^2=NHEt	40	1000	4	50	1	0.0090	MW, DSC	274
	40	1000	10	50	1	0.022	MW, DSC	274
	40	1000	400	50	1	0.147	MW, DSC	274
M=Zr								
L^1=$(NEt_2)_2$, L^2=NHEt	40	1000	100	50	1	0.198	MW, DSC	274
	40	1000	400	50	1	0.159	MW, DSC	274
	40	1000	1000	50	1	0.140	MW, DSC	274
	40	1000	3 [f]	50	1	0.050	MW, DSC	274
	40	1000	10 [f]	50	1	0.307	MW, DSC	274
2.8. (Tp)MX								
M=Ti, X=Cl_3								
Tp=Tp	5	25	200	40	1	0.28		249
	5	25	1000	40	1	0.41	MW	249
	5	25	5000	40	1	0.35	MW	249
	5	25	1000	60	1	0.19	MW	249
Tp=Tp*	5	25	200	40	1	0.10		249
	5	25	1000	40	1	0.50		249
	5	25	1000	60	1	0.19	MW	249
M=Zr, X=Cl_3								
Tp=Tp	10	50	50	40	1	0.79	MW	249
	10	50	100	60	1	0.83	MW	249
Tp=Tp*	10	50	100	40	1	7.3	MW	249
3. Other Catalyst Systems								
3.1 Acenaphtyl Substituted Cyclopentadienyl Complexes								
[η^5-7,9-Ph_2Cyclopenta[*a*]acenaphthadienyl]$_2ZrCl_2$	3.0	9.4	2000	30	2.8	4.40	MW, DSC	93
	3.0	9.4	2000	50	3.8	11.80	MW, DSC	93
[1,2-(η^5-7,9-Ph_2Cyclopenta[*a*]acenaphthadienyl)-1-phenyl]$_2$ethane$ZrCl_2$	3.0	9.4	2000	70	4.6	12.60	MW, DSC	93
	3.0	9.4	2000	30	2.8	5.20	MW, DSC	93
	3.0	9.4	2000	50	3.8	8.10	MW, DSC	93
[1-(η^5-7,9-Ph_2Cyclopenta[*a*]acenaphthadienyl)-2-Ph-2-(η^5-9-Flu)]ethane$ZrCl_2$	3.0	9.4	2000	70	4.6	19.10	MW, DSC	93
	2.0	9.4	2000	30	2.8	82.60	MW, DSC	93
	2.0	9.4	2000	50	3.8	154.00	MW, DSC	93
	2.0	9.4	2000	70	4.6	118.00	MW, DSC	93
3.2. Phenylboratobenzene Zirconium Complexes								
$(C_5H_5B\text{-}N(^iPr)_2)_2ZrCl_2$								
$(C_5H_5B\text{-}Ph)_2ZrCl_2$	21	955	450	25	1	0.69		283
	21	955	490	25	1	oligomers	GC-MS	283
$(4\text{-}^tBuC_5H_4B\text{-}Ph)_2ZrCl_2$	21	955	490	60	21	1.180	MW	283
$[Cp(CpC_2H_2NMe_2.HCl)TiCl_2]_2O$	2.5	50	4000	20	1	47.36	MW, DSC	245

Table 5 (cont.)

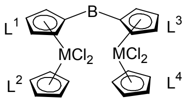
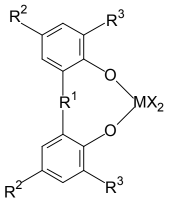
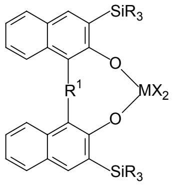
Metallocene	Polymerisation Conditions mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[M]^c	T/ °C	P/ Bar ^{d}	Activity/ $\times 10^5$g PE (mol M h)$^{-1}$	Anal.^{e}	Ref.
3.3. Bimetallic Catalysts								
(μ-$C_{12}H_8$[SiPh(Ind)$_2$ZrCl_2]$_2$)	(n.g.)	1.0	1000	40	1	114	NMR,MW, DSC	262
	(n.g.)	1.0	1000	60	2	448	NMR,MW, DSC	262
	(n.g.)	1.0	1000	80	1	690	NMR,MW, DSC	262
	(n.g.)	1.0	1000	100	1	707	NMR,MW, DSC	262
Sn[Cp_2Zr(NMe_2)$_2$]$_2$	9.5	(n.g.)	600	70	7	38.6	η	173
[$L^1M^1Cl_2L^2$]B[$L^3M^2Cl_2L^4$]								
B=C(CH_2)$_2$								
$M^1=M^2=$Zr; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	4.58	MW, DSC	284
$M^1=M^2=$Hf; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	1.84	MW, DSC	284
$M^1=M^2=$Zr; $L^1=L^2=L^4=$Cp, $L^3=$1-Ind	6.25	29.7	2500	30	2	9.29	MW, DSC	284
$M^1=$Zr, $M^2=$Hf; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	6.34	MW, DSC	284
$M^1=$Zr, $M^2=$Rh; $L^1=L^2=L^3=$Cp; $L^4=$COD (no Cl's attached to Rh)	6.25	29.7	2500	30	2	7.85	MW, DSC	284
$M^1=$Zr, $M^2=$Hf; $L^1=L^2=L^3=$Cp; $L^4=$COD (no Cl's attached to Rh)	6.25	29.7	2500	30	2	2.14	MW, DSC	284
$M^1=$Zr, $M^2=TiCl_3$; $L^1=L^2=L^3=$Cp (no L^4, replaced with Cl)	6.25	29.7	2500	30	2	8.72	MW, DSC	284
B=C(Me)$_2$								
$M^1=M^2=$Zr; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	3.42	NMR,MW	285
$M^1=$Zr, $M^2=$Hf; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	2.70	NMR,MW	285
$M^1=M^2=$Hf; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	1.53	NMR,MW	285
$M^1=$Zr, $M^2=$Co; $L^1=L^2=$Cp, $L^4=Cp^*$; $L^3=$Ind (no Cl's attached to Co)	6.25	29.8	(n.g.)	30	2	41.68	NMR,MW	285
$M^1=$Zr, $M^2=$Rh; $L^1=L^2=L^3=$Cp; $L^4=(CO)_2$ (no Cl's attached to Rh)	6.25	29.8	(n.g.)	30	2	1.20	NMR,MW	285
$M^1=$Zr, $M^2=$Rh; $L^1=L^2=$Cp; $L^3=$Ind; $L^4=(CO)_2$ (no Cl's attached to Rh)	6.25	29.8	(n.g.)	30	2	1.36	NMR,MW	285
$M^1=$Zr, $M^2=$Mn; $L^1=L^2=$Cp; $L^3=$Ind; $L^4=(CO)_3$ (no Cl's attached to Mn)	6.25	29.8	(n.g.)	30	2	2.19	NMR,MW	285
B=C(CH_2)$_5$								
$M^1=M^2=$Zr; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	6.71	NMR,MW	285
$M^1=$Zr, $M^2=$Hf; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	3.63	NMR,MW	285
$M^1=M^2=$Hf; $L^1=L^2=L^4=$Cp, $L^3=$Ind	6.25	29.8	(n.g.)	30	2	0.94	NMR,MW	285
B=C[4-^{t}Bu(CH_2)$_5$]								
$M^1=$Zr, $M^2=$Rh; $L^1=L^2=$Cp; $L^3=$Ind; $L^4=(CO)_2$ (no Cl's attached to Rh)	6.25	29.8	(n.g.)	30	2	0.45	NMR,MW	285
B=SiMe_2								
$M^1=M^2=$Hf; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	0.25	NMR,MW	286
$M^1=M^2=$Zr; $L^1=L^2=L^4=$Cp, $L^3=$1-Ind	6.25	29.7	2500	30	2	0.31	NMR,MW	286
$M^1=M^2=$Zr; $L^1=L^4=$Cp, $L^2=L^3=$1-Ind	6.25	29.7	2500	30	2	0.866	NMR,MW	286
$M^1=$Zr, $M^2=$Hf; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	0.145	NMR,MW	286
$M^1=$Zr, $M^2=$Ti; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	0.170	NMR,MW	286
$M^1=$Zr, $M^2=$Ti; $L^1=L^2=L^3=$Cp, $L^4=Cp^*$	6.25	29.7	2500	30	2	0.186	NMR,MW	286
$M^1=$Zr, $M^2=$Ti; $L^1=L^2=L^3=$Cp, $L^4=Cl_3$	6.25	29.7	2500	30	2	0.330	NMR,MW	286
$M^1=$Zr, $M^2=$Zr; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	0.290	NMR,MW	286
B=-Si(Me)$_2$-(CH_2)$_2$-(Me)$_2$Si-								
$M^1=M^2=$Zr; $L^1=L^2=L^3=L^4=$Cp	6.25	29.7	2500	30	2	0.10	NMR,MW	286

Table 5 (cont.)

	Polymerisation Conditions					Activity/		
Metallocene	mol M/ $\times 10^{-6}$mol [a]	[M]/ $\times 10^{-6}$M [b]	[Al]:[M] [c]	T/ °C	P/ Bar [d]	$\times 10^5$g PE (mol M h)$^{-1}$	Anal. [e]	Ref.
4. ML^1L^2								
4.1. General catalyts								
M=Ti, $L^1=Cl_2$								
$L^2=1,8\text{-}C_{10}H_6(NSiMe_3)_2$	10	200	500	r.t.	1	0.20	DSC	287
$L^2=1,8\text{-}C_{10}H_6(NSi(^iPr)_3)_2$	10	200	500	r.t.	1	0.126	DSC	287
$L^2=1,8\text{-}C_{10}H_6(NSi(Me)_2(^tBu))_2$	21.4	71.3	1000	60	4	1.92	MW	288
$L^2=Me_3SiNCH_2CH_2NSiMe_3$	31	311	100	0	2.8	0.095		289
	31	311	100	21	2.8	0.081		289
	31	311	100	50	2.8	0.098		289
	4670	51888	1000	25	1	0.124		253
	4670	51888	2000	25	1	0.103		253
	4670	51888	3000	25	1	0.0956		253
M=Ti, $L^1=Cl_2$, $L^2={}^iPrNC(Ph)N{}^iPr$	8.79	4400	200	25	1	1.2	DSC	290
M=Zr, $L^1=Cl_2$								
$L^2=1,8\text{-}C_{10}H_6(NSi(^iPr)_3)_2$	10	200	500	RT	1	0	DSC	287
$L^2=Me_3SiNCH_2CH_2NSiMe_3$	5490	61000	1000	25	1	0.0723		253
	5490	61000	2000	25	1	0.0578		253
	5490	61000	3000	25	1	0.0568		253
L^1=none, $L^2=[Me_3SiNCH_2CH_2NSiMe_3]_2$	3020	33555	1000	25	1	0.0361		253
	3020	33555	2000	25	1	0.0124		253
	3020	33555	3000	25	1	0.0108		253
$L^2={}^iPrNC(Ph)N{}^iPr$	8.79	4400	800	0	1	0.14	DSC	290
	8.79	4400	200	25	1	0.068	DSC	290
	8.79	4400	400	25	1	0.34	DSC	290
	8.79	4400	800	25	1	0.56	DSC	290
	8.79	4400	2000	25	1	0.60	DSC	290
	8.79	4400	400	60	1	0.86	DSC	290
	8.79	4400	800	60	1	2.1	DSC	290
	8.79	4400	1000	60	1	1.8	DSC	290
	8.79	4400	2000	60	1	4.0	DSC	290
$L^2=[(SiMe_3)NC(Ph)N(SiMe_3)]_2$	8.7	290	396	5	1	0.065	MW, DSC	291
	8.7	290	196	25	1	0.32	MW, DSC	291
	8.7	290	793	25	1	0.24	MW, DSC	291
	8.7	290	396	25	5	28.5	MW, DSC	291
	8.7	290	396	60	1	0.28	MW, DSC	291
$L^2=[(SiMe_3)NC(4\text{-}MePh)N(SiMe_3)]_2$	8.7	290	396	25	1	0.16	MW, DSC	291
$L^2=N(Si{}^iPr_3)(2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}2\text{-}C_6H_4)\text{-}(Si{}^iPr_3)N$	7.31	731	500	22	1	52.74	MW	292
M=Zr, $L^1=(Me)_2$								
$L^2=N(Si{}^iPr_3)(2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}2\text{-}C_6H_4)\text{-}(Si{}^iPr_3)N$	7.77	777	500	0	1	12.58	MW	292
$L^2=(2,6\text{-}Me_2\text{-}C_6H_3)MeSiNCH_2CH_2N\text{-}SiMe(2,6\text{-}Me_2\text{-}C_6H_3)$	(n.g.)	(n.g.)	750	50	10	0.40		293
M=Zr, $L^1=(NMe_2)_2$								
$L^2=(2,6\text{-}Me_2\text{-}$C6H3)NH(SiPh$_2$)NH (2,6-Me$_2$-$C_6H_3$) + $HNMe_2$	(n.g.)	(n.g.)	750	50	10	0.30		293
$L^2=(2,6\text{-}Me_2\text{-}C_6H_3)MeSi\text{-}NCH_2CH_2NSiMe(2,6\text{-}Me_2\text{-}C_6H_3)$	(n.g.)	(n.g.)	750	25	10	25.0		293
	(n.g.)	(n.g.)	750	50	10	49.0		293
	(n.g.)	(n.g.)	750	75	10	68.0		293
	(n.g.)	(n.g.)	100	50	10	14.0		293
	(n.g.)	(n.g.)	2000	50	10	99.0		293
	(n.g.)	(n.g.)	750	50	10	7.0		293

Table 5 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Anal.[e]	Ref.
	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[M][c]	T/ °C	P/ Bar [d]	$\times10^{5}$g PE (mol M h)$^{-1}$		
4.2. Biphenoxide And Binaphtoxide Catalysts								
[2,2'-R^1(4-R^2-6-$R^3C_6H_2$-O)$_2$]MX_2								
<u>M=Ti</u>								
R^1=none, R^2=OMe, R^3=^{t}Bu, X_2=(same ligand)	0.5	2.5	500	20	3	0.60		294
R^1=rings joined, R^2=OMe, R^3=^{t}Bu, X_2=$(CH_2Ph)_2$	0.4	2.0	500	20	3	0.18		294
R^1=CH_2, R^2=Et, R^3=^{t}Bu, X_2=$(CH_2Ph)_2$	0.2	1.0	500	20	3	1.80		294
R^1=CH_2, R^2=Et, R^3=^{t}Bu, X_2=Cl_2	0.2	1.0	500	20	3	3.90		294
R^1=S, R^2=Me, R^3=^{t}Bu, X_2=Cl_2	0.2	1.0	500	20	3	47.40	MW	294
<u>M=Zr</u>								
R^1=S, R^2=Me, R^3=^{t}Bu, X_2=Cl_2	0.2	1.0	500	20	3	0		294
[1,1'-(2,2',3,3'-$OC_{10}H_5SiR_3$)]$_2MX_2$								
<u>M=Ti</u>								
R_3=Me_3, X_2=$(CH_2Ph)_2$	0.2	1.0	500	40	3	1.80	MW, DSC	294
R_3=Ph_3, X_2=$(CH_2Ph)_2$	0.2	1.0	500	20	3	0		294
<u>M=Zr</u>								
R_3=Me_3 , X_2=Cl_2	0.54	2.7	500	20	3	1.52	MW, DSC	294
R_3=$MePh_2$, X_2=Cl_2.	0.38	1.9	500	20	3	2.03	MW, DSC	294
R_3=$MePh_2$, X_2=$(CH_2Ph)_2$	0.2	1.0	500	20	3	10.50		294
R_3=Ph_3, X_2=$(CH_2Ph)_2$	0.2	1.0	500	20	3	0		294
R_3=Ph_3, X_2=$(CH_2SiMe_3)_2$	0.2	1.0	500	20	3	0.46		294
R_3=Ph_3, X_2=Cl_2	0.2	1.0	500	20	3	2.75		294
R_3=Ph_3, X_2=Me_2	0.2	1.0	500	20	3	0.45		294

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[a] The molar amount of Group 4 metal, M, used in the polymerisation.

[b] The final concentration of M in the polymerisation vessel. If this value cannot be obtained from the original publication, this is indicated in the relevant field as n.g. (not given).

[c] Ratio of co-catalyst catalyst metal. Unless otherwise stated, the co-catalyst employed is MAO.

[d] The assumption that 1 bar ≈ 1 atm has been made.

[e] Analysis performed on the polymer obtained from the polymerisation. MW = Molecular Weight, NMR = ^{13}C NMR spectroscopy, DSC = Differential Scanning Calorimetry, IR = Infra-Red, GC-MS = Gass Chromotography-Mass Spectrometry.

[f] Aluminium in the form of TIBA.

Table 6 Propene polymerisation reactions of Group 4 metallocene / Aluminoxane catalysts.

Metallocene	Polymerisation Conditions					Activity/	Analysis^{e}	Ref
	mol M/ $\times 10^{-6}$mol^{a}	[M]/ $\times 10^{-6}$M^{b}	[Al]:[Zr]^{c}	T/ °C	P/ Bar^{d}	$\times 10^{4}$g PP/ (mol M h)$^{-1}$		
1. Metallocenes with two cyclopentadienyl-type ligands								
1.1. (Cp^{1})(Cp^{2})MX								
M=Ti, X=Cl$_2$								
Cp^{1}=Cp^{2}=Cp	2.5	50	4000	20	1.4	0.986	MW	245
Cp^{1}=Cp, Cp^{2}=(C$_2$H$_4$Nme$_2$)Cp	2.5	50	4000	20	1.4	10	MW	245
Cp^{1}=Cp^{2}=1,2-(CH$_2$)$_{10}$Cp	15	60	5000	-30	1.2	1.32	MW	87
	15	60	5000	25	1.2	3.36	MW	87
M=Zr, X=Cl$_2$								
Cp^{1}=Cp^{2}=(1,3,3,5,5-pentamethyl-cyclohexyl)Cp	50.0	238	(n.g.)	30	2	0.23	NMR	251
Cp^{1}=Cp=(1-Ph-2,3-Me$_2$)Cp	5	50	1000	20	3.4	365.7	NMR, MW, DSC, IR	128
	5	50	1000	20	5.2	451.1	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	879.7	NMR, MW, DSC, IR	128
Cp^{1}=Cp^{2}=[1-(4-MePh)-2,3-Me$_2$]Cp	5	50	1000	20	3.4	232.5	NMR, MW, DSC, IR	128
	5	50	1000	20	5.2	323.5	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	712.0	NMR, MW, DSC, IR	128
Cp^{1}=Cp^{2}=[1-(2-Naph)-2,3-Me$_2$]Cp	5	50	1000	20	3.4	86.7	NMR, MW, DSC, IR	128
	5	50	1000	20	5.2	102.7	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	283.3	NMR, MW, DSC, IR	128
Cp^{1}=Cp^{2}=1,2-(CH$_2$)$_{10}$Cp	15	60	5000	-30	1.2	25.2	MW	87
	7.5	30	5000	25	1.2	48.0	MW	87
M=Hf, X=Cl$_2$								
Cp^{1}=Cp^{2}=1,2-(CH$_2$)$_{10}$Cp	32	128	2500	-30	1.2	0.648	MW	87
	15	60	5000	25	1.2	1.33	MW	87
M=Zr, X=[-P(SiMe$_3$)$_2$]$_2$								
Cp^{1}=Cp^{2}=Cp	8.68	289	2700	30	1.0	6.2	NMR	295
M=Zr, X=-PH(2,4,6-^{i}Pr$_3$Ph) + Cl								
Cp^{1}=Cp^{2}=Cp	8.68	289	2700	30	1.0	2.2	NMR	295
M=Zr, X=-[PH(2,4,6-^{i}Pr$_3$Ph)]$_2$								
Cp^{1}=Cp^{2}=Cp	8.68	289	2700	30	1.0	3.8	NMR	295
M=Zr, X=Me$_3$SiNCH$_2$CH$_2$NSiMe$_3$								
	3540	39333	1000	25	1	109	NMR	253
	3540	39333	2000	25	1	199	NMR	253
	3540	39333	3000	25	1	122	NMR	253
1.2. B(Cp^{1})(Cp^{2})MX								
M=Ti, B=SiMe$_2$, X=Cl$_2$								
Cp^{1}=Cp, Cp^{2}=3-(SiMe$_3$)Cp	9.5	19	290	40	l.p.	0.1	NMR, MW, DSC	254
Cp^{1}=Cp^{2}=3-(SiMe$_3$)Cp (*meso*)	9.5	19	290	40	l.p.	0	NMR, MW, DSC	254

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[Zr]^c	T/ ^{o}C	P/ Bar ^{d}	$\times$ 10^{4}g PP/ (mol M h)$^{-1}$		
M=Zr, B=SiMe$_2$, X=Cl$_2$								
Cp^1=Cp, Cp^2=3-(SiMe$_3$)Cp	9.5	19	290	40	l.p.	1.27	NMR, MW, DSC	254
Cp^1=Cp^2=3-(SiMe$_3$)Cp (*rac*)	9.5	19	290	40	l.p.	0.59	NMR, MW, DSC	254
	9.5	19	290	50	l.p.	0.61	NMR, MW, DSC	254
	9.5	19	5000	50	l.p.	0.86	NMR, MW, DSC	254
Cp^1=Cp^2=2,4-Me$_2$Cp	0.2	6.7	10000	25	3	628	NMR, MW	197
Cp^1=Cp^2=2-Me-4-^{i}PrCp	6.25	(n.g.)	1200	50	2	2900	NMR, DSC, MW	201
Cp^1=Cp^2=2-Me-4-^{t}BuCp	6.25	(n.g.)	1200	50	2	36.0	NMR, DSC, MW	201
M=Zr, B= -SiMe$_2$(CHCH$_2$), X=Cl$_2$								
Cp^1=Cp^2=2,4-Me$_2$Cp	0.2	6.7	10000	25	3	1600	NMR, MW	197
	0.1	3.33	10000	23	3	1314	NMR, MW, DSC	296
Cp^1=Cp^2=spirosilacyclohexane[*b*]^{i}Pr Cp	6.25	(n.g.)	1200	50	2	420.0	NMR, DSC, MW	201
Cp^1=Cp^2=spirosilacyclohexane[*b*]^{t}Bu Cp	6.25	(n.g.)	1200	50	2	200.0	NMR, DSC, MW	201
M=Zr, B=LRh-(η^2-(CHCH$_2$)$_3$Si-), X=Cl$_2$								
L=Ind	0.1	3.33	10000	23	3	2256	NMR, MW, DSC	296
L=Cp	0.1	3.33	10000	23	3	1854	NMR, MW, DSC	296
L=Cp*	0.1	3.33	10000	23	3	2259	NMR, MW, DSC	296
M=Hf, B=SiMe$_2$, X=Cl$_2$								
Cp^1=Cp, Cp^2=3-(SiMe$_3$)Cp	9.5	19	290	40	l.p.	0.20	NMR, MW, DSC	254
	9.5	19	290	50	l.p.	0.46	NMR, MW, DSC	254
	9.5	19	5000	0	l.p.	0.42	NMR, MW, DSC	254
1.3. B^{1}B^2(Cp^1)(Cp^2)MX								
M=Zr, X=Cl$_2$								
B^1=B^2=-SiMe$_2$; Cp^1=Cp^2=3,4-Me$_2$Cp	6.25	15.6	1216	50	l.p.	0		198
B^1=B^2=-SiMe$_2$; Cp^1=Cp^2= 4-CHMe$_2$Cp	7	(n.g.)	1200	0	l.p.	164.2	NMR, MW	297
B^1=B^2=-SiMe$_2$; Cp^1=Cp^2= 3,5-(CHMe$_2$)$_2$Cp	7	(n.g.)	1200	0	l.p.	18.88	NMR, MW	297
B^1=B^2=-SiMe$_2$; Cp^1=4-CHMe$_2$Cp; R^2=3,5-(CHMe$_2$)$_2$Cp	7	(n.g.)	1200	0	l.p.	93.05	NMR, MW	297
1.4. (Ind^1)(Ind^2) MX								
M=Zr, X=Cl$_2$								
Ind^1=Ind^2=2-MeInd	(n.g.)	(n.g.)	3500	0	1	445	NMR, MW	259
Ind^1=Ind^2=2-^{i}PrInd	(n.g.)	(n.g.)	3500	0	1	34	NMR, MW	259
Ind^1=Ind^2=2-^{n}BuInd	(n.g.)	(n.g.)	3500	0	1	66	NMR, MW	259
Ind^1=Ind^2=2-BzInd	(n.g.)	(n.g.)	3500	0	1	1.7	NMR, MW	259
Ind^1=Ind^2=2-PhInd	5	50	1000	20	5.2	170.0	NMR, MW	126
	5.5	50	1000	25	1.7	38	NMR, MW	125
	5	50	1000	20	2.4	95.2	NMR, MW	127
	5.5	50	1000	25	2.4	51	NMR, MW	125
	5	50	1000	20	3.4	83.2	NMR, MW	127
	5	50	1000	20	3.4	138	NMR, MW, DSC, IR	128

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis [e]	Ref
	mol M/ $\times 10^{-6}$mol [a]	[M]/ $\times 10^{-6}$M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	$\times 10^4$g PP/ (mol M h)$^{-1}$		
Ind^1=Ind^2=2-PhInd (cont.)	5.5	50	1000	25	3.4	88	NMR, MW, DSC, IR	125
	5	50	1000	0	5.1	154.4	NMR, MW	127
	5	50	1000	20	5.1	148	NMR, MW	127,128
	5.5	50	1000	25	5.1	171	NMR, MW	125
	5.5	50	1000	25	6.2	240	NMR, MW	125
	5	50	1000	20	6.9	96.0	NMR, MW	127
	5	50	1000	20	l.p.	252.5	NMR, MW, DSC, IR	128
	6	50	1000	20	l.p.	248.0	NMR, MW	132
	0.5	5	1000	(n.g.)	l.p.	275.6	NMR, MW, DSC, IR	131
	5	50	1000	40	l.p.	410.4	NMR, MW, IR	136
Ind^1=Ind^2=2-CyInd	5	50	1000	20	3.4	37.4	NMR, MW, DSC, IR	128
	5	50	1000	20	5.1	60.2	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	234.0	NMR, MW, DSC, IR	128
	(n.g.)	(n.g.)	3500	0	1	28	NMR, MW	259
Ind^1=Ind^2=2-(3,5-Me$_2$Ph)Ind	5	50	1000	25	2.4	15	NMR, MW	125
	5	50	1000	25	3.4	22	NMR, MW, DSC, IR	125
	5	50	1000	25	5.1	36	NMR, MW	125
	5	50	1000	25	6.2	54	NMR, MW	125
Ind^1=Ind^2=2-[3,5-F(Me)$_3$Ph]Ind	5	50	1000	25	1.7	25	NMR, MW	125,127
	5	50	1000	20	2.4	20.6	NMR, MW	127
	5	50	1000	25	2.4	50	NMR, MW	125,127
	5	50	1000	20	3.4	58.2	NMR, MW	127
	5	50	1000	25	3.4	73	NMR, MW, DSC, IR	125,127
	5	50	1000	20	5.1	62.4	NMR, MW	127
	5	50	1000	25	5.1	135	NMR, MW	125,127
	5	50	1000	20	6.9	63.8	NMR, MW	127
Ind^1=Ind^2=2-[(4-Me)Ph]Ind	5	50	1000	20	1.7	84.2	NMR, MW	130
	5	50	1000	20	3.4	129.0	NMR, MW	130
	5	50	1000	20	5.1	147.4	NMR, MW	130
	5	50	1000	20	l.p.	200.1	NMR, MW	130
Ind^1=Ind^2=2-[(4-Et)Ph]Ind	5	50	1000	20	1.7	78.0	NMR, MW	130
	5	50	1000	20	3.4	154.4	NMR, MW	130
	5	50	1000	20	5.1	236.4	NMR, MW	130
	5	50	1000	20	l.p.	239.0	NMR, MW	130
Ind^1=Ind^2=2-[(4-^{n}Bu)Ph]Ind	5	50	1000	20	1.7	69.7	NMR, MW	130
	5	50	1000	20	3.4	128.9	NMR, MW	130
	5	50	1000	20	5.1	232.2	NMR, MW	130
	5	50	1000	20	l.p.	244.0	NMR, MW	130
Ind^1=Ind^2=2-[(4-^{t}Bu)Ph]Ind	5	50	1000	20	1.7	57.8	NMR, MW	130
	5	50	1000	20	3.4	117.4	NMR, MW	130
	5	50	1000	20	5.1	201.9	NMR, MW	130
	5	50	1000	20	l.p.	269.8	NMR, MW	130
	5	50	1000	20	l.p.	235.6	NMR, MW	130
	5	50	1000	20	l.p.	231.4	NMR, MW	130
Ind^1=Ind^2=2-[(4-SiMe$_3$)Ph]Ind	5	50	1000	20	1.7	78.6	NMR, MW	130
	5	50	1000	20	3.4	134.4	NMR, MW	130
	5	50	1000	20	5.1	226.9	NMR, MW	130
	5	50	1000	20	l.p.	251.0	NMR, MW	130

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis [e]	Ref
	mol M/ ×10^{-6}mol [a]	[M]/ ×10^{-6}M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	× 10^4g PP/ (mol M h)$^{-1}$		
Ind^1=Ind^2=2-[(4-CF$_3$)Ph]Ind	5	50	1000	20	1.7	77.5	NMR, MW	130
	5	50	1000	20	3.4	128.1	NMR, MW	130
	5	50	1000	20	5.1	170.4	NMR, MW	130
	5	50	1000	20	l.p.	263.1	NMR, MW	130
Ind^1=Ind^2=2-(4-ClPh)Ind	5	50	1000	20	1.7	33.1	NMR, MW	130
	5	50	1000	20	3.4	68.9	NMR, MW	130
	5	50	1000	20	5.1	114.1	NMR, MW	130
	5	50	1000	20	l.p.	333.3	NMR, MW	130
Ind^1=Ind^2=1-Me-2-PhInd (*meso*-isomer)	5	50	1000	20	5.2	14.0	NMR, MW	126
	5	50	1000	20	l.p.	14.0	NMR, MW	126
	6	50	1000	20	l.p.	14.0	NMR, MW	132
Ind^1=Ind^2=1-Me-2-PhInd (*rac*-isomer)	5	50	1000	20	5.2	22.0	NMR, MW	126
	5	50	1000	20	l.p.	36.0	NMR, MW	126
	6	50	1000	20	l.p.	25.0	NMR, MW	132
Ind^1=IndH$_4$, Ind^2=2-CyInd	5	50	1000	20	3.4	53.1	NMR, MW, DSC, IR	128
	5	50	1000	20	5.2	95.7	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	339.4	NMR, MW, DSC, IR	128
Ind^1=IndH$_4$, Ind^2=CyInd	5	50	1000	20	3.4	94.0	NMR, MW, DSC, IR	128
	5	50	1000	20	5.2	202.0	NMR, MW, DSC, IR	128
	5	50	1000	20	l.p.	239.0	NMR, MW, DSC, IR	128
Ind^1=2-PhInd, Ind^2=2-(3,5-CF$_3$ Ph)Ind	6	50	1000	20	l.p.	144.0	NMR, MW	132
Ind^1=Ind^2=2-(3,5-CF$_3$Ph)Ind	6	50	1000	20	l.p.	300.0	NMR, MW	132
Ind^1=Ind^2=2-(3,5-Me$_2$ Ph)Ind	6	50	1000	20	l.p.	78.0	NMR, MW	132
Ind^1=(1-Me-2-Ph)Ind, Ind^2=2-(3,5-Me$_2$Ph)Ind	6	50	1000	20	l.p.	181.0	NMR, MW	132
Ind^1=(1-Me-2-CF$_3$Ph)Ind, Ind^2=2-(3,5-Me$_2$Ph)Ind	6	50	1000	20	l.p.	103.0	NMR, MW	132
Ind^1=(1-Me-2-Ph)Ind, Ind^2=2-PhInd	6	50	1000	20	l.p.	280.0	NMR, MW	132
Ind^1=(1-Me-2-CF$_3$Ph)Ind, Ind^2=2-PhInd	6	50	1000	20	l.p.	135.0	NMR, MW	132
Ind^1=Ind^2=2-[3,5-(OMe)$_2$Ph]Ind	5	50	1000	0	l.p.	18.8	NMR, MW, IR	136
	5	50	1000	20	l.p.	44.1	NMR, MW, IR	136
	5	50	1000	40	l.p.	68.9	NMR, MW, IR	136
Ind^1=Ind^2=2-(4-NMe$_2$Ph)Ind	5	50	1000	0	l.p.	31.1	NMR, MW, IR	136
	5	50	1000	20	l.p.	33.2	NMR, MW, IR	136
	5	50	1000	40	l.p.	88.3	NMR, MW, IR	136
Ind^1=Ind^2=2-(3,5-^{t}Bu$_2$-4-OMe)Ind	5	50	1000	0	l.p.	66.8	NMR, MW, IR	136
	5	50	1000	20	l.p.	257.8	NMR, MW, IR	136
	5	50	1000	40	l.p.	660.0	NMR, MW, IR	136
Ind^1=Ind^2=2-(-CpFeCp)Ind	5	50	1000	0	l.p.	76.3	NMR, MW, IR	136
	5	50	1000	20	l.p.	88.5	NMR, MW, IR	136
	5	50	1000	40	l.p.	60.7	NMR, MW, IR	136

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/		
	mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[Zr]^c	T/ ^{o}C	P/ Bar ^{d}	$\times$ 10^{4}g PP/ (mol M h)$^{-1}$	Analysis ^{e}	Ref
Ind^1=Ind^2=2-(1-adamantyl)Ind	5	50	1000	0	l.p.	0.6	NMR, MW, IR	136
M=Zr, X=Br$_2$								
Ind^1=Ind^2=2-PhInd	6	50	1000	20	l.p.	249.0	NMR, MW	132
Ind^1=Ind^2=2-(3,5-CF$_3$Ph)Ind	6	50	1000	20	l.p.	274.0	NMR, MW	132
Ind^1=2-PhInd, Ind^2=2-(3,5-CF$_3$Ph)Ind	6	50	1000	20	l.p.	114.0	NMR, MW	132
Ind^1=2-(3,5-CF$_3$Ph)Ind, Ind^2=2-(3,5-Me$_2$Ph)Ind	6	50	1000	20	l.p.	218.0	NMR, MW	132
Ind^1=2-PhInd, Ind^2=2-(3,5-Me$_2$Ph)Ind	6	50	1000	20	l.p.	147.0	NMR, MW	132
M=Hf, X=Cl$_2$								
Ind^1=Ind^2=2-PhInd	5	50	1000	20	2.4	108.0	NMR, MW	127
	5	50	1000	0	3.4	116.0	NMR, MW	127
	5	50	1000	20	3.4	146.0	NMR, MW	127
	5	50	1000	20	5.2	144.0	NMR, MW	127
	5	50	1000	20	6.9	118.0	NMR, MW	127
Ind^1=Ind^2=2-[(3,5-F(Me)$_3$Ph)]Ind	5	50	1000	20	2.41	50.6	NMR, MW	127
	5	50	1000	25	2.41	113.0	NMR, MW	127
	5	50	1000	20	3.4	36.0	NMR, MW	127
	5	50	1000	25	3.4	135.0	NMR, MW	127
	5	50	1000	20	5.2	66.0	NMR, MW	127
	5	50	1000	25	5.2	219.0	NMR, MW	127
	5	50	1000	20	6.9	70.0	NMR, MW	127
	5	50	1000	25	6.9	305.0	NMR, MW	127
1.5. B(Ind^1)(Ind^2)MX$_2$ M=Zr, X$_2$=Cl, B=CR^{1}CR^2								
CR^{1}CR^2=C$_2$H$_4$, Ind^1=Ind^2=Ind	0.48	(n.g.)	8000	20	l.p.	1820	NMR, MW, DSC	151
	0.48	(n.g.)	8000	30	l.p.	3560	NMR, MW, DSC	151
	0.48	(n.g.)	8000	40	l.p.	5800	NMR, MW, DSC	151
	0.48	(n.g.)	8000	50	l.p.	13960	NMR, MW, DSC	151
	0.48	(n.g.)	8000	60	l.p.	13640	NMR, MW, DSC	151
	0.48	(n.g.)	8000	70	l.p.	25170	NMR, MW, DSC	151
	2	6.66	2000	1	2 mol	800.0	MW, NMR	89
CR^{1}CR^2=C$_2$H$_4$, Ind^1=Ind^2=IndH$_4$	2	6.66	2000	1	2 mol	110.0	MW, NMR	89
CR^{1}CR^2=C$_2$H$_4$, Ind^1=Ind^2=2-OSi(Me)$_2$(^{t}Bu)Ind	11	55.0	3000	0	1.30	50.0	NMR, MW, DSC	261
	11	55.0	3000	20	2.00	530.0	NMR, MW, DSC	261
	11	55.0	3000	40	2.70	900.0	NMR, MW, DSC	261
	11	55.0	3000	60	3.40	700.0	NMR, MW, DSC	261
	11	55.0	3000	80	4.10	350.0	NMR, MW, DSC	261
	11	55.0	50	40	2.70	20.0	NMR, MW, DSC	261

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis [e]	Ref
	mol M/ ×10^{-6}mol [a]	[M]/ ×10^{-6}M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	× 10^{4}g PP/ (mol M h)$^{-1}$		
CR^{1}CR^{2}=C$_{2}$H$_{4}$, Ind^{1}=Ind^{2}=2-OSi(Me)$_{2}$(^{t}Bu)Ind (cont.)	11	55.0	250	40	2.70	850.0	NMR, MW, DSC	261
	11	55.0	500	40	2.70	990.0	NMR, MW, DSC	261
	11	55.0	1000	40	2.70	940.0	NMR, MW, DSC	261
	11	55.0	10000	40	2.70	1020.0	NMR, MW, DSC	261
CR^{1}CR^{2}=C$_{2}$H$_{4}$, Ind^{1}=Ind^{2}=2-OSi(Me)$_{2}$(^{t}Bu)IndH$_{4}$	11	55.0	3000	20	2.00	2.0	NMR, MW, DSC	261
	11	55.0	3000	40	2.70	15.0	NMR, MW, DSC	261
	11	55.0	3000	60	3.40	50.0	NMR, MW, DSC	261
	11	55.0	500	40	2.70	41.0	NMR, MW, DSC	261
	11	55.0	10000	40	2.70	16.0	NMR, MW, DSC	261
Ind^{1}=Ind^{2}=Ind								
CR^{1}CR^{2}=CH$_{2}$CH(Me)	(n.g.)	(n.g.)	500-5000	50	1.4	401	NMR, MW	214
CR^{1}CR^{2}=*trans*-cyclopentylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	134	NMR, MW	214
CR^{1}CR^{2}=*trans*-cyclohexylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	282	NMR, MW	214
CR^{1}CR^{2}=*trans*-cycloheptylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	175	NMR, MW	214
CR^{1}CR^{2}=*trans*-cyclooctylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	42	NMR, MW	214
-Ind^{1}=Ind^{2}=IndH$_{4}$								
CR^{1}CR^{2}=1,2-propylene	(n.g.)	(n.g.)	500-5000	50	1.4	355	NMR, MW	214
CR^{1}CR^{2}=*trans*-cyclopentylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	83	NMR, MW	214
CR^{1}CR^{2}=*trans*-cycloheptylene (*rac* + *meso*)	(n.g.)	(n.g.)	500-5000	50	1.4	113	NMR, MW	214
M=Zr, X=Cl$_{2}$, B=CH$_{2}$								
Ind^{1}=Ind^{2}=3-(^{t}Bu)Ind	(n.g.)	(n.g.)	1000	50	l.p.	3740	NMR, MW, DSC	153
	(n.g.)	(n.g.)	8000	60	l.p.	12340	NMR, MW, DSC	153
M=Zr, X=Cl$_{2}$, B=CMe$_{2}$								
Ind^{1}=Ind^{2}=Ind	0.46	(n.g.)	8000	0	l.p.	89.0	NMR, MW, DSC	151
	0.46	(n.g.)	8000	20	l.p.	1020	NMR, MW, DSC	151
	0.46	(n.g.)	8000	40	l.p.	5000	NMR, MW, DSC	151
	2.31	(n.g.)	8000	50	l.p.	6580	NMR, MW, DSC	151
	0.46	(n.g.)	8000	60	l.p.	12570	NMR, MW, DSC	151
	0.23	(n.g.)	8000	70	l.p.	14510	NMR, MW, DSC	151
	0.092	2.29	5000	50	l.p.	4430	NMR, MW	152
	0.092	2.29	5000	50	l.p.	8130	NMR, MW	152 [g]

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[Zr]^c	T/ ^{o}C	P/ Bar ^{d}	$\times$ 10^{4}g PP/ (mol M h)$^{-1}$		
Ind^1=Ind^2=3-(Me)Ind	8.96	(n.g.)	8000	0	l.p.	85.0	NMR, MW, DSC	151
	1.12	(n.g.)	8000	20	l.p.	280	NMR, MW, DSC	151
	1.12	(n.g.)	8000	35	l.p.	1010	NMR, MW, DSC	151
	0.45	(n.g.)	8000	50	l.p.	2840	NMR, MW, DSC	151
	0.45	(n.g.)	8000	70	l.p.	8130	NMR, MW, DSC	151
Ind^1=Ind^2=3-(^{t}Bu)Ind	0.37	(n.g.)	8000	20	l.p.	3200	NMR, MW, DSC	151
	0.37	(n.g.)	8000	30	l.p.	6880	NMR, MW, DSC	151
	0.37	(n.g.)	8000	40	l.p.	11240	NMR, MW, DSC	151
	0.18	(n.g.)	8000	50	l.p.	12460	NMR, MW, DSC	151
	0.37	(n.g.)	8000	60	l.p.	16060	NMR, MW, DSC	151
	0.18	(n.g.)	8000	70	l.p.	11000	NMR, MW, DSC	151
Ind^1=Ind^2=3-(SiMe$_3$)Ind	6.93	(n.g.)	8000	20	l.p.	960	NMR, MW, DSC	151
	0.87	(n.g.)	8000	30	l.p.	3900	NMR, MW, DSC	151
	6.93	(n.g.)	8000	40	l.p.	1420	NMR, MW, DSC	151
	0.87	(n.g.)	8000	50	l.p.	7360	NMR, MW, DSC	151
	0.52	(n.g.)	8000	60	l.p.	5940	NMR, MW, DSC	151
	0.52	(n.g.)	8000	70	l.p.	4360	NMR, MW, DSC	151
M=Zr, X$_2$=Cl, B=SiMe$_2$								
Ind^1=Ind^2=Ind	0.50	1.35	15800	50	2	1400	NMR, MW, DSC	94
	0.5	1.25	15800	50	2	1400	NMR, MW, DSC	98
	0.8	1	15000	70	2	1400	MW, DSC	97
	0.8	1	15000	70	5	3500	MW, DSC	97
	5	0.5	15000	70	l.p.	19000	NMR, MW, DSC	97
	6.3	0.63	12000	70	l.p.	19000	NMR, MW, DSC	298
100% *rac*	0.5	5	1000	(n.g.)	l.p.	623.4	NMR, MW	131
100% *meso*	0.5	5	1000	(n.g.)	l.p.	105.0	NMR	131
Ind^1=Ind^2=2-MeInd	0.50	1.35	15800	50	2	920.0	NMR, DSC, MW	94
	0.5	1.25	15800	50	2	920.0	NMR, MW, DSC	98
	6.3	0.63	12000	70	l.p.	10200	NMR, MW, DSC	298
	0.8	1	15000	70	5	4200	MW, DSC	97
Ind^1=Ind^2=3-^{t}Bu-Ind	2	6.66	2000	1	2 mol	260.0	MW, NMR	89
Ind^1=Ind^2=2-(NMe$_2$)Ind	6.25	16.9	1200	50	2	40.0	NMR, DSC, MW	299
Ind^1=Ind^2=2-PhInd	15	60	1000	50	1.2	19.05	NMR, MW, DSC	300
	15	60	1000	25	1.2	38.33	NMR, MW, DSC	300

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ $\times10^{-6}$mol ^{a}	[M]/ $\times10^{-6}$M ^{b}	[Al]:[Zr]^c	T/ ^{o}C	P/ Bar ^{d}	$\times$ 10^4g PP/ (mol M h)$^{-1}$		
Ind^1=Ind^2=2-PhInd (cont.)	15	60	10000	0	1.2	5.90	NMR, MW, DSC	300
100% *rac*	0.5	5	1000	(n.g.)	l.p.	240.8	NMR, MW, DSC, IR	131
100% *meso*	0.5	5	1000	(n.g.)	l.p.	409.2	NMR, MW, DSC, IR	131
42% *rac*	0.5	5	1000	(n.g.)	l.p.	240.0	NMR, MW, DSC, IR	131
57% *rac*	0.5	5	1000	(n.g.)	l.p.	317.2	NMR, MW, DSC, IR	131
61% *rac*	0.5	5	1000	(n.g.)	l.p.	305.2	NMR, MW, DSC, IR	131
75% *rac*	0.5	5	1000	(n.g.)	l.p.	268.0	NMR, MW, DSC, IR	131
Ind^1=Ind^2=3-PhInd	20	80	2000	25	1.2	12.63	NMR, MW, DSC	300
	20	80	2000	0	1.2	6.17	NMR, MW, DSC	300
	20	80	2000	-30	1.2	0.70	NMR, MW, DSC	300
Ind^1=Ind^2=4-PhInd	6.3	0.63	12000	70	l.p.	5500	NMR, MW, DSC	298
	5	0.5	15000	70	l.p.	4800	NMR, MW, DSC	97
Ind^1=Ind^2=2-Me-4-^{i}PrInd	5	0.5	15000	70	l.p.	24500	NMR, MW, DSC	97
	0.8	1	15000	70	2	4900	MW, DSC	97
	0.8	1	15000	70	5	13400	MW, DSC	97
Ind^1=Ind^2=2-Me-4-PhInd	0.8	1	15000	70	2	11100	MW, DSC	97
	0.8	1	15000	70	5	18200	MW, DSC	97
	6.3	0.63	12000	70	l.p.	76500	NMR, MW, DSC	298
	3	0.3	15000	70	l.p.	75500	NMR, MW, DSC	97
Ind^1=Ind^2=2-Me-5-Ph-Ind	0.8	1	15000	70	5	1100	MW, DSC	97
	5	0.5	15000	70	l.p.	6300	NMR, MW, DSC	97
Ind^1=Ind^2=2-Me-4-(1-Naph)	3	0.3	15000	70	l.p.	8750	NMR, MW, DSC	97
Ind^1=Ind, Ind^2=2-Me-4-PhInd	6.3	0.63	12000	70	l.p.	50300	NMR, MW, DSC	298
Ind^1=Ind, Ind^2=2-Me-4-PhInd	6.3	0.63	12000	70	l.p.	44600	NMR, MW, DSC	298
Ind^1=Ind^2= benz[*e*]indenyl	0.5	1.25	15800	50	1	520.0	NMR, MW, DSC	98
	0.50	1.35	15800	50	2	2460	NMR, DSC, MW	94
	0.5	1.25	15800	50	3	5340	NMR, MW, DSC	98
	0.5	1.25	15800	50	7	28770	NMR, MW, DSC	98
	5	0.5	15000	70	l.p.	27400	NMR, MW, DSC	97
Ind^1=Ind^2= 2-methylbenz[*e*]indenyl	0.5	1.25	15800	50	1	170.0	NMR, MW, DSC	98
	0.5	1.25	15800	50	2	900.0	NMR, MW, DSC	98
	0.50	1.35	15800	50	2	900.0	NMR, DSC, MW	94
	0.8	1	15000	70	2	9200	MW, DSC	97

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ ×10^{-6}mol ^{a}	[M]/ ×10^{-6}M ^{b}	[Al]:[Zr]^c	T/ °C	P/ Bar ^{d}	× 10^{4}g PP/ (mol M h)$^{-1}$		
Ind^1=Ind^2= 2-methylbenz[*e*]indenyl (cont.)	0.5	1.25	15800	50	3	1170	NMR, MW, DSC	98
	0.8	1	15000	70	5	19400	MW, DSC	97
	0.5	1.25	15800	50	5	14500	NMR, MW, DSC	98
	5	0.5	15000	70	l.p.	40300	NMR, MW, DSC	97
(Ind^1)=(Ind^2)= cyclopenta[*c*]phenanthryl	0.50	1.35	15800	50	2	580.0	NMR, DSC, MW	94
(Ind^1)=(Ind^2)=cyclopenta[*l*]phenanthryl	1.35	3.64	3100	50	2	2410.0	NMR, DSC, MW	94
(Ind^1)=(Ind^2)=2-methylcyclopenta[*l*]phenanthryl	1.16	3.14	1300	50	2	5560.0	NMR, DSC, MW	94
(Ind^1)=(Ind^2)=2-methyltetrahydrobenz[*e*]indenyl	3.25	8.78	2600	50	2	2870.0	NMR, DSC, MW	94
M=Zr, B=Si(Me)(Ph)								
Ind^1=Ind^2=2-Me-4-PhInd	5	0.5	15000	70	l.p.	55300	NMR, MW, DSC	97
M=Zr, B= -SiMe$_2$-O-Me$_2$Si-								
Ind^1=Ind^2=Ind	2.5	50	4000	-50	1.03	14.4	MW, DSC	263
	2.5	50	4000	-20	1.03	22.4	MW, DSC	263
	2.5	50	4000	0	1.03	28.8	MW, DSC	263
	2.5	50	4000	20	1.03	57.6	MW, DSC	263
M=Zr, B=B(L)								
Ind^1=Ind^2=Ind, L=Ph + PMe$_3$	(n.g.)	30	1000	20	2	32.6	NMR, MW	166
	(n.g.)	30	220	40	2	78.3	NMR, MW	166
	(n.g.)	30	1000	40	2	105.2	NMR, MW	166
	(n.g.)	30	5000	40	2	123.2	NMR, MW	166
	(n.g.)	30	1000	60	2	174	NMR, MW	166
Ind^1=Ind^2=Ind, L=Ph + OEt$_2$	(n.g.)	30	1000	r.t.	2	1.0-7.5	MW	166
1.6. B^{1}B^2(Ind^1)(Ind^2)MX								
M=Zr, X=Cl$_2$								
B^1=B^2=-SiMe$_2$; Ind^1=Ind^2=IndH$_4$	6.25	15.6	1216	50	l.p.	0		198
1.7. B(Ind)(Cp)MCl$_2$								
M=Ti, B=CMe$_2$								
Ind=Ind, Cp=Cp	2	6.66	2000	1	2 mol	73.0	NMR, MW	89
Ind=3-^{t}Bu-Ind, Cp=3-^{t}Bu-Cp (*threo*)	2	6.66	2000	1	2 mol	195.0	NMR, MW	89
M=Ti, B=-CPh$_2$								
Ind=Ind, Cp=Cp	0.20	20	1000	18	2	0.6	NMR, MW	155
M=Zr, B=CMe$_2$								
Ind=Ind, Cp=Cp	0.10	1	1000	-78	2	0.2	NMR, MW	155
	0.10	10	1000	18	2	9.4	NMR, MW	155
Ind=3-Me-Ind, Cp=3-^{t}Bu-Cp (*threo*)	2	6.66	2000	1	2	130.0	NMR, MW	89
	2	6.66	2000	1	2	130.0	NMR, MW	89
Ind=3-^{t}Bu-Ind, Cp=3-^{t}Bu-Cp (*threo*)	2	6.66	2000	1	2	9270.0	NMR, MW	89
	2	6.66	2000	30	2	200.0	NMR, MW	89
	2	6.66	2000	60	2l	4200.0	NMR, MW	89
Ind=3-^{t}Bu-Ind, Cp=3-^{t}Bu-Cp (*erythro*)	2	6.66	2000	1	2	6.0	NMR, MW	89

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis [e]	Ref
	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	$\times$ 10^4g PP/ (mol M h)$^{-1}$		
Ind=1-tolylInd, Cp=Cp	12	48	2000	25	1.2	5.0 [f]	NMR, MW	157
	12	48	2000	-30	1.2	1.0 [f]	NMR, MW	157
M=Zr, B=SiMe$_2$								
Ind=1-(tolyl)Ind, Cp=Cp	15	48	2000	25	1.2	13.2 [f]	NMR, MW	157
	15	48	2000	-30	1.2	3.0 [f]	NMR, MW	157
Ind=2-(tolyl)Ind, Cp=Cp	15	48	2000	25	1.2	157.0 [f]	NMR, MW	157
	15	48	2000	-30	1.2	80.0 [f]	NMR, MW	157
Ind=3-^{t}Bu-Ind, Cp=3-^{t}Bu-Cp (*threo*)	2	6.66	2000	1	2	11.0	NMR, MW	89
	2	6.66	2000	30	2	190.0	NMR, MW	89
M=Zr, B=-CPh$_2$								
Ind=Ind, Cp=Cp	0.20	20	1000	-78	2	0.3	NMR, MW	155
	0.20	20	1000	18	2	9.1	NMR, MW	155
M=Zr, B=-Cy								
Ind=Ind, Cp=Cp	0.20	20	1000	-78	2	0.3	NMR, MW	155
	0.20	20	1000	18	2	9.7	NMR, MW	155
M=Zr, B=PPh								
Ind^1=Ind^2=2-Me-4-PhInd	1	200	37000	50	l.p.	1824	NMR, MW, DSC	171
	1	200	37000	67	l.p.	5256	NMR, MW, DSC	171
	4	800	1000	67	l.p.	1012	NMR, MW, DSC	171
	4	800	8000	50	l.p.	1678	NMR, MW, DSC	171
	4	800	8000	50	l.p.	2928 [g]	NMR, MW, DSC	171
M=Zr, B=^{i}PrP								
Ind^1=Ind^2=2-Me-4-PhInd	4	800	8186	30	l.p.	1715	NMR	171
	1	200	8004	50	l.p.	4516	NMR	171
	1	200	8016	50	l.p.	8812 [g]	NMR	171
	1	200	37600	50	l.p.	11540	NMR	171
M=Hf, B=-CPh$_2$								
Ind=Ind, Cp=Cp	0.20	20	1000	-40	2	1.0	NMR, MW	155
	0.20	20	1000	0	2	2.5	NMR, MW	155
	0.20	20	1000	18	2	6.2	NMR, MW	155
	0.20	20	1000	50	2	14.0	NMR, MW	155
	0.20	20	1000	80	2	25.6	NMR, MW	155
M=Hf, B=-Cy								
Ind=Ind, Cp=Cp	0.20	20	1000	-40	2	0.4	NMR, MW	155
	0.20	20	1000	0	2	6.6	NMR, MW	155
	0.20	20	1000	18	2	7.0	NMR, MW	155
	0.20	20	1000	50	2	8.8	NMR, MW	155
	0.20	20	1000	80	2	21.4	NMR, MW	155
1.8. (Flu^1)(Flu^2)MCl$_2$								
M=Zr								
Flu^1=Flu^2=1-MeFlu	9.6	9.6	(n.g.)	25	l.p.	750	NMR, DSC	301
1.9. B(Flu^1)(Flu^2)MCl$_2$								
M=Zr, B=SiMe$_2$								
Flu^1=Flu^2=Flu	1	1	500	50	l.p.	1605	NMR	171
Flu^1=Flu, Flu^2=2,7-^{t}Bu$_2$Flu	(n.g.)	(n.g.)	1000	70	l.p.	3020	NMR, MW	170
M=Zr, B=-PPh								
Flu^1=Flu^2=Flu	1	1	500	50	l.p.	73	NMR	171

Table 6 (cont.)

	Polymerisation Conditions					Activity/		
Metallocene	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	$\times 10^4$g PP/ (mol M h)$^{-1}$	Analysis [e]	Ref
1.10. B(Cp)(Flu)MCl$_2$								
M=Zr,B=-CH$_2$								
Cp=Cp, Flu=Flu	2.5-5.0	5.0-9.9	(n.g.)	60	l.p.	4150	NMR, MW	302
Cp=Cp, Flu=2,7-Br$_2$Flu	1.8-3.6	3.6-7.1	(n.g.)	60	l.p.	4030	NMR, MW	302
M=Zr,B=-CMe$_2$								
Cp=Cp, Flu=Flu	1	1	500	67	l.p.	3648	NMR, MW	171
	1.1	1.1	(n.g.)	50	l.p.	1769	NMR, MW, DSC	303
Cp=3-^{t}BuCp, Flu=Flu	13.9	(n.g.)		20	l.p.	10kg.g^{-1}	NMR, MW, DSC	304
	3.48	(n.g.)		40	l.p.	18kg.g^{-1}	NMR, MW, DSC	304
	3.48	(n.g.)		60	l.p.	48 kg.g^{-1}	NMR, MW, DSC	304
	3.48	(n.g.)		80	l.p.	20 kg.g^{-1}	NMR, MW, DSC	304
Cp=Cp, Flu=2,7-Me$_2$Flu	2.2-4.3	4.3-8.7	(n.g.)	60	l.p.	1120	NMR, DSC	305
Cp=Cp, Flu=2,7-Ph$_2$Flu	1.7-3.4	3.4-6.8	(n.g.)	60	l.p.	1760	NMR, DSC	305
Cp=Cp, Flu=2,7-Mes$_2$Flu	15-3.0	3.0-6.0	(n.g.)	60	l.p.	7710	NMR, DSC	305
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	1.8-3.7	3.7-7.4	(n.g.)	60	l.p.	5480	NMR, DSC	305
Cp=Cp, Flu=2,7-(MeO)$_2$Flu	2.0-4.1	4.1-8.1	(n.g.)	60	l.p.	30	NMR, DSC	305
Cp=Cp, Flu=2,7-Cl$_2$Flu	2.0-4.0	4.0-8.0	(n.g.)	60	l.p.	2070	NMR, DSC	305
Cp=Cp, Flu=2,7-Br$_2$Flu	1.7-3.4	3.4-6.8	(n.g.)	60	l.p.	2680	NMR, DSC	305
M=Zr, B=C(H)(Ph)								
Cp=Cp, Flu=Flu	2.1-4.2	4.2-8.2	(n.g.)	60	l.p.	5710	NMR, MW, DSC	306
Cp=Cp, Flu=2,7-Ph$_2$Flu	1.6-3.2	3.2-6.3	(n.g.)	60	l.p.	2990	NMR, MW, DSC	306
M=Zr, B=C(Me)(Ph)								
Cp=Cp, Flu=2,7-Ph$_2$Ph	1.5-3.1	3.1-6.2	(n.g.)	60	l.p.	5180	NMR, MW, DSC	306
M=Zr, B=cyclopentyl								
Cp=Cp, Flu=Flu	2.2-4.4	4.4-8.7	(n.g.)	60	l.p.	3530	NMR, MW, DSC	306
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	1.8-3.5	3.5-7.0	(n.g.)	60	l.p.	2350	NMR, MW, DSC	306
Cp=Cp, Flu=2,7-(Mes)$_2$Flu	1.4-2.9	2.9-5.8	(n.g.)	60	l.p.	4270	NMR, MW, DSC	306
M=Zr, B=cyclohexyl								
Cp=Cp, Flu=Flu	2.2-4.2	4.2-8.5	(n.g.)	60	l.p.	7920	NMR, MW, DSC	306
M=Zr, B=-CPh$_2$								
Cp=Cp, Flu=Flu	2.35	2.35	(n.g.)	50	l.p.	622.1	NMR, MW, DSC	303
Cp=Cp, Flu=2,7-Me$_2$Flu	1.7-3.4	3.4-6.8	(n.g.)	60	l.p.	3470	NMR, DSC	305
Cp=Cp, Flu=2-PhFlu	1.6-3.2	3.2-6.5	(n.g.)	60	l.p.	2450	NMR, DSC	305
Cp=Cp, Flu=2,7-Ph$_2$Flu	1.4-2.8	2.8-5.6	(n.g.)	60	l.p.	3540	NMR, DSC	305
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	1.5-3.0	3.0-6.0	(n.g.)	60	l.p.	3180	NMR, DSC	305
Cp=Cp, Flu=2,7-(PhMe$_2$C)$_2$Flu	1.3-2.5	2.5-5.0	(n.g.)	60	l.p.	7270	NMR, DSC	305
Cp=Cp, Flu=2,7-(MeO)$_2$Flu	1.6-3.2	3.2-6.5	(n.g.)	60	l.p.	40	NMR, DSC	305
Cp=Cp, Flu=2,7-Cl$_2$Flu	2.0-4.0	4.0-8.0	(n.g.)	60	l.p.	4100	NMR, DSC	305
M=Zr, B=-CH$_2$CH$_2$								
Cp=Cp, Flu=Flu	10	67	2000	25	1.2	64.2	NMR, MW, DSC	307

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/		
	mol M/ ×10^{-6}mol^{a}	[M]/ ×10^{-6}M^{b}	[Al]:[Zr]^{c}	T/ ^{o}C	P/ Bar^{d}	× 10^{4}g PP/ (mol M h)$^{-1}$	Analysis^{e}	Ref
Cp=Cp, Flu=Flu (cont.)	10	67	2000	50	1.2	104.2	NMR, MW, DSC	307
	10	67	2000	70	1.2	217.5	NMR, MW, DSC	307
	10	67	2000	90	1.2	151.7	NMR, MW, DSC	307
Cp=CpMe$_4$, Flu=Flu								
	10	67	2000	25	1.2	7.5	NMR, NMR, DSC	307
	10	67	2000	50	1.2	17.5	NMR, MW, DSC	307
	10	67	2000	70	1.2	81.7	NMR, MW, DSC	307
M=Zr, B=-PPh	10	67	2000	90	1.2	29.2	NMR, MW, DSC	307
Cp=Cp, Flu=Flu	1	1	500	50	l.p.	912	NMR, MW	171
	1	1	500	67	l.p.	1414	NMR, MW	171
M=Zr, B=-SiMe$_2$								
Cp=Cp, Flu=Flu	1	1	500	67	l.p.	164	NMR, MW	171
	(n.g.)	(n.g.)	1000	70	l.p.	2540	NMR, MW	170
	1.25	25	3000	0	0.69	727	NMR, DSC, MW	272
	1.25	25	2400	25	0.69	685	NMR, DSC, MW	272
	1.25	25	2000	50	0.69	589	NMR, DSC, MW	272
Cp=Cp, Flu=2,7-^{t}BuFlu	(n.g.)	(n.g.)	1000	70	l.p.	16640	NMR, MW	170
M=Zr, B=SiPh$_2$								
Cp=Cp, Flu=Flu	(n.g.)	(n.g.)	1000	70	l.p.	11740	NMR, MW	170
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	(n.g.)	(n.g.)	1000	70	l.p.	9640	NMR, MW	170
M=Zr, B=GePh$_2$								
Cp=Cp, Flu=Flu	(n.g.)	(n.g.)	1000	70	l.p.	828	NMR, MW	170
M=Zr, B=C(Me)((CH$_2$)$_2$CHCH$_3$)								
Cp=Cp, Flu=Flu	2.1-4.2	4.2-8.5	2500	60	l.p.	66.20	NMR, MW	270
M=Hf								
B=-CMe$_2$, Cp=Cp, Flu=Flu	7.9	7.9	(n.g.)	50	l.p.	963.8	NMR, MW, DSC	303
M=Hf, B=-CPh$_2$								
Cp=Cp, Flu=Flu	8.6	8.6	(n.g.)	50	l.p.	208.8	NMR, MW, DSC	303
Cp=Cp, Flu=2,7-Ph$_2$Flu	1.3-2.5	2.5-5.0	(n.g.)	60	l.p.	1570	NMR, DSC	305
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	1.3-2.6	2.6-5.3	(n.g.)	60	l.p.	1370	NMR, DSC	305
M=Zr, B=cyclopentyl								
Cp=Cp, Flu=2,7-^{t}Bu$_2$Flu	1.5-3.0	3.0-6.1	(n.g.)	60	l.p.	1170	NMR, MW, DSC	306
1.11. B(Ind)(Flu)MCl$_2$								
M=Zr, B=CH$_2$CH$_2$								
Ind=2-MeInd, Flu=Flu	1.25	25	4000	20	2	31.6	NMR	268
	1.25	25	4000	70	2	21.2	NMR, DSC	268
Ind=4,7-Me$_2$Ind, Flu=Flu	1.25	25	4000	20	2	32.0	NMR	268
	1.25	25	4000	70	2	8.0	NMR	268
Ind=2,4,7-Me$_3$Ind, Flu=Flu	1.25	25	4000	20	2	68	NMR, MW, DSC	268
	1.25	25	4000	70	2	34	NMR, MW, DSC	268

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ $\times 10^{-6}$mol ^{a}	[M]/ $\times 10^{-6}$M ^{b}	[Al]:[Zr] ^{c}	T/ °C	P/ Bar ^{d}	$\times 10^4$g PP/ (mol M h)$^{-1}$		
M=Zr, B=SiMe$_2$								
Ind=Ind, Flu=Flu	5.0	100	1000	50	0.69	24.6	NMR, DSC, MW	272
2. Metallocenes with one cyclopentadienyl-type ligand								
2.1. (η^5-CpR)ML								
M=Ti								
Cp=Cp, R=none, L=Cl$_3$	2.5	50	4000	20	1.4	0		245
Cp=Cp*, R=none, L=Cl$_3$	2.5	50	4000	20	1.4	0		245
Cp=Cp, R=C$_2$H$_4$NMe$_2$, L=Cl$_3$	2.5	50	4000	20	1.4	143	MW	245
Cp=CpMe$_4$, R=C$_2$H$_4$NMe$_2$, L=Cl$_3$	2.5	50	4000	20	1.4	11.0	MW	245
Cp=Me$_4$Cp, R=Si(Me$_2$)N(CHMePh), L=Cl$_2$	3.4	34	350	30	3.4	0.325	NMR, MW	308
	3.4	34	350	30	l.p.	0.188	NMR, MW	308
Cp=Me$_4$Cp, R=Si(Me$_2$)N(^{t}Bu), L=Cl$_2$	3.8	38	289	30	3.4	0.820	NMR, MW	308
	3.8	38	289	30	l.p.	0.380	NMR, MW	308
M=Ti, L=(O-^{i}Pr)$_3$								
Cp=Cp, R=(CH$_2$)$_2$NMe$_2$	2.5	50	2000	50	(n.g.)	6.4	MW	277
Cp=Cp, R=(CH$_2$)$_2$N(^{i}Pr)$_2$	2.5	50	2000	25	(n.g.)	1.76		277
M=Ti, L=[N(Et)$_2$]$_2$								
Cp=CpMe$_4$, R=SiMe$_2$NCH$_2$CH$_2$Si(OCH$_3$)$_3$	(n.g.)	(n.g.)	800	20	1.5	0.5	MW, DSC	281
	(n.g.)	(n.g.)	800	20	l.p.	0.37	MW, DSC	281
2.2. (η^5-1-IndR)ML								
M=Ti								
Ind=Ind, R=Si(Me$_2$)N^{t}Bu, L=Cl$_2$	3.9	39	350	30	3.4	0.056	NMR, MW	308
	3.9	39	350	30	l.p.	0.019	NMR, MW	308
	3.9	39	1000	30	3.4	0.203	NMR, MW	308
	3.9	39	1000	30	l.p.	0.190	NMR, MW	308
Ind=Ind, R=(CH$_2$)$_2$NMe$_2$, L=Cl$_3$	2.5	50	2000	21	(n.g.)	48.4	MW	277
Ind=Ind, R=Si(Me$_2$)N(CHMePh), L=Cl$_2$	3.4	34	350	30	3.4	0.072	NMR, MW	308
	3.4	34	350	30	l.p.	0.196	NMR, MW	308
Ind=Ind, R=Si(Me$_2$)N(Cy), L=Cl$_2$	3.6	36	400	30	3.4	0.063	NMR, MW	308
	3.6	36	400	30	l.p.	0.239	NMR, MW	308
M=Ti, L=(O-^{i}Pr)$_3$								
Ind=Ind, R=(CH$_2$)$_2$NMe$_2$	2.5	50	2000	21	(n.g.)	21.3	MW	277
Ind=Ind, R=(CH$_2$)$_2$N(^{i}Pr)$_2$	2.5	50	2000	21	(n.g.)	0	MW	277
Ind=Ind, R=(CH$_2$)$_2$-2-C$_5$H$_4$N	2.5	50	2000	21	(n.g.)	traces	MW	277
2.3. (η^5-9-FluR)ML								
M=Zr, L=Cl$_2$								
Flu=Flu, R=Si(Me$_2$)N(^{t}Bu)	4.6	46	350	30	3.4	0.031	NMR, MW	308
	4.6	46	350	30	l.p.	0.017	NMR, MW	308

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/	Analysis [e]	Ref
	mol M/ ×10^{-6}mol [a]	[M]/ ×10^{-6}M [b]	[Al]:[Zr] [c]	T/ °C	P/ Bar [d]	× 10^{4}g PP/ (mol M h)$^{-1}$		
3. Other metallocene catalysts								
3.1 Acenaphtyl Substituted Cyclopentadienyl Complexes								
[η^5-7,9-Ph$_2$Cyclopenta[*a*]acenaphthadienyl]$_2$ZrCl$_2$	6	18.8	2000	50	4.6	3.5	MW, NMR	93
	6	18.8	2000	50	5.7	5.3	MW, NMR	93
[1,2-(η^5-7,9-Ph$_2$Cyclopenta[*a*]acenaphthadienyl)-1-phenyl]$_2$-ethaneZrCl$_2$	6	18.8	2000	50	4.6	30.0	MW, NMR	93
	6	18.8	2000	50	5.7	40.0	MW, NMR	93
[1-(η^5-7,9-Ph$_2$Cyclopenta[*a*]acenaphthadienyl)-2-Ph-2-(η^5-9-Flu)]ethaneZrCl$_2$	6	18.8	2000	50	1.4	40.0	MW, NMR	93
	6	18.8	2000	50	2.0	75.0	MW, NMR	93
	6	18.8	2000	50	4.6	248.0	MW, NMR	93
	6	18.8	2000	50	5.7	1030.0	MW, NMR	93
3.2. Phospholyl Catalysts								
(Phos1)(Phos2)ZrCl$_2$								
Phos1 = Phos2 = 3,4-Me$_2$Phos	10.0	44.7	500	45	6	0		309
=2,3,4,5-Me$_4$Phos	10.0	44.7	500	45	6	0		309
=2,5-^{n}Pr$_2$Phos	10.0	44.7	500	45	6	73.8	MW	309
=2,5-^{i}Pr$_2$Phos	10.0	44.7	500	45	6	332	MW	309
=2,5-^{c}Pr$_2$Phos	10.0	44.7	500	45	6	951	MW	309
=2,5-^{c}Pe$_2$Phos	10.0	44.7	500	45	6	1052	MW	309
=2,5-^{t}Bu$_2$Phos	10.0	44.7	500	45	6	0		309
=2,5-(SiMe$_3$)$_2$Phos	10.0	44.7	500	45	6	0		309
=2-Ph-5-MePhos	10.0	44.7	500	45	6	841	MW	309
=2-Ph-5-^{n}PrPhos	10.0	44.7	500	45	6	757	MW	309
=2-Ph-5-^{c}PePhos	10.0	44.7	500	45	6	993	MW	309
=2,5-Ph$_2$Phos	10.0	44.7	500	45	6	1547	MW	309
=2,5-Ph$_2$-3-MePhos	10.0	44.7	500	45	6	756	MW	309
=2,5-Ph$_2$-3,4-Me$_2$Phos	10.0	44.7	500	45	6	139	MW	309
=2,3,4,5-Ph$_4$Phos	10.0	44.7	500	45	6	0		309
=2-An-5-MePhos	10.0	44.7	500	45	6	504	MW	309
=2-Phen-5-MePhos	10.0	44.7	500	45	6	294	MW	309
(Phos)(Cp)ZrCl$_2$								
Phos=3,4-Me$_2$Phos	10.0	44.7	500	45	6	0		309
Phos=2,3,4,5-Me$_4$Phos	10.0	44.7	500	45	6	0		309
Phos=2,5-^{t}BuPhos	10.0	44.7	500	45	6	71	MW	309
Phos=2,5-Ph$_2$Phos	10.0	44.7	500	45	6	588	MW	309
3.3. Bimetallic Catalysts								
(Cp)$_2$Zr{μ-PSiMe$_3$}$_2$Mo(CO)$_4$	6.38	212	2700	30	1.0	5.2	NMR	295
(Cp)$_2$Zr{μ-PSiMe$_3$}$_2$Ni(CO)$_2$	6.38	212	2700	30	1.0	8.4	NMR	295
(Cp)$_2$Zr{μ-AsSiMe$_3$}$_2$Cr(CO)$_4$	6.38	212	2700	30	1.0	6.1	NMR	295
(CpMe)$_2$Zr{μ-P-2,4,6-^{i}Pr$_3$C$_6$H$_2$}$_2$Mo(CO)$_4$	6.38	212	2700	30	1.0	3.2	NMR	295
(CpMe)$_2$Zr{μ-P-2,4,6-^{i}Pr$_3$C$_6$H$_2$}$_2$Cr(CO)$_4$	6.38	212	2700	30	1.0	1.2	NMR	295
R-[-SiMe(Ind)$_2$ZrCl$_2$]$_2$								
R=(CH$_2$)$_2$, Ind=2-Me-4-PhInd	6.3	0.63	12000	70	l.p.	5000	NMR, MW, DSC	298
R=(CH$_2$)$_6$, Ind=2-Me-4-PhInd	6.3	0.63	12000	70	l.p.	9300	NMR, MW, DSC	298

Table 6 (cont.)

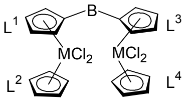
Metallocene	Polymerisation Conditions					Activity/	Analysis ^{e}	Ref
	mol M/ ×10^{-6}mol ^{a}	[M]/ ×10^{-6}M ^{b}	[Al]:[Zr]^c	T/ ^{o}C	P/ Bar ^{d}	× 10^{4}g PP/ (mol M h)$^{-1}$		
$[L^1M^1Cl_2L^2]C(CH_2)_2[L^3M^2Cl_2L^4$								
B=C(CH$_2$)$_2$								
M^1=M^2=Zr; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	7.44	NMR, MW, DSC	284
M^1=M^2=Hf; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	5.71	NMR, MW, DSC	284
M^1=M^2=Zr; L^1=L^2=L^4=Cp, L^3=1-Ind	31.3	149	2500	30	2	18.2	NMR, MW, DSC	284
M^1=Zr, M^2=Hf; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	8.0	NMR, MW, DSC	284
M^1=Zr, M^2=Rh; L^1=L^2=L^3=Cp; L^4=COD, (no Cl's attached to Rh)	31.3	149	2500	30	2	5.1	NMR, MW, DSC	284
M^1=Zr, M^2=TiCl$_3$; L^1=L^2=L^3=Cp	31.3	149	2500	30	2	3.0	NMR, MW, DSC	284
B=C(Me)$_2$								
M^1=M^2=Zr; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	1.11	NMR, MW	285
M^1=Zr, M^2=Hf; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	0.21	NMR, MW	285
M^1=M^2=Hf; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	0.67	NMR, MW	285
M^1=Zr, M^2=Co; L^1=L^2=Cp, L^4=Cp*, L^3=Ind, (no Cl's attached to Co)	0.5	2.38	(n.g.)	30	2	19.2	NMR, MW	285
M^1=Zr, M^2=Rh; L^1=L^2=L^3=Cp; L^4=(CO)$_2$, (no Cl's attached to Rh)	0.5	2.38	(n.g.)	30	2	1.95	NMR, MW	285
M^1=Zr, M^2=Rh; L^1=L^2=Cp; L^3=Ind; L^4=(CO)$_2$, (no Cl's attached to Rh)	0.5	2.38	(n.g.)	30	2	0.11	NMR, MW	285
M^1=Zr, M^2=Mn; L^1=L^2=Cp; L^3=Ind; L^4=(CO), (no Cl's attached to Mn)	0.5	2.38	(n.g.)	30	2	0.13	NMR, MW	285
B=C(CH$_2$)$_5$								
M^1=M^2=Zr; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	1.37	NMR, MW	285
M^1=Zr, M^2=Hf; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	1.14	NMR, MW	285
M^1=M^2=Hf; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	1.02	NMR, MW	285
B=C[4-^{t}Bu(CH$_2$)$_5$]								
M^1=M^2=Zr; L^1=L^2=L^4=Cp, L^3=Ind	0.5	2.38	(n.g.)	30	2	4.63	NMR, MW	285
M^1=Zr, M^2=Rh; L^1=L^2=Cp; L^3=Ind; L^4=(CO)$_2$, (no Cl's attached to Rh)	0.5	2.38	(n.g.)	30	2	0.21	NMR, MW	285
B=SiMe$_2$								
M^1=M^2=Hf; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	0.73	NMR, MW	286
M^1=M^2=Zr; L^1=L^2=L^4=Cp, L^3=1-Ind	31.3	149	2500	30	2	0.32	NMR, MW	286
M^1=M^2=Zr; L^1=L^4=Cp, L^2=L^3=1-Ind	31.3	149	2500	30	2	0.25	NMR, MW	286
M^1=Zr, M^2=Hf; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	0.18	NMR, MW	286
M^1=Zr, M^2=Ti; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	0.73	NMR, MW	286
M^1=Zr, M^2=Ti; L^1=L^2=L^3=Cp, L^4=Cp*	31.3	149	2500	30	2	0.35	NMR, MW	286
M^1=Zr, M^2=Ti; L^1=L^2=L^3=Cp, L^4=Cl$_3$	31.3	149	2500	30	2	0.19	NMR, MW	286
M^1=Zr, M^2=Zr; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	0.84	NMR, MW	286
B=-Si(Me)$_2$-(CH$_2$)$_2$-(Me)$_2$Si-								
M^1=M^2=Zr; L^1=L^2=L^3=L^4=Cp	31.3	149	2500	30	2	0.28	NMR, MW	286

Table 6 (cont.)

Metallocene	Polymerisation Conditions					Activity/		
	mol M/ $\times10^{-6}$mol [a]	[M]/ $\times10^{-6}$M [b]	[Al]:[Zr][c]	T/ °C	P/ Bar [d]	$\times$ 10^4g PP/ (mol M h)$^{-1}$	Analysis [e]	Ref
4. MXX'								
M=Ti, X=Cl$_2$, X'=^{i}PrNC(Ph)N^{i}Pr	8.79	4400	400	25	1	0.95	NMR	290
M=Zr, X=Cl$_2$, X'=^{i}PrNC(Ph)N^{i}Pr	8.79	4400	400	25	1	0.68	NMR	290
	8.79	4400	1000	25	1	1.4	NMR	290
	8.79	4400	4000	25	1	2.1	NMR	290
	8.79	4400	1000	60	1	2.1	NMR	290
	8.79	4400	2000	60	1	1.4	NMR	290

[a] The molar amount of Group 4 metal, M, used in the polymerisation.

[b] The final concentration of M in the polymerisation vessel. If this value cannot be obtained from the original publication, this is indicated in the relevant field as n.g. (not given).

[c] Ratio of co-catalyst:catalyst metal. Unless otherwise stated, the co-catalyst employed is MAO.

[d] The assumption that 1 bar ≈ 1 atm has been made. Polymerisation's performed in liquid propene are indicated as l.p.

[e] Analysis performed on the polymer obtained from the polymerisation. MW = Molecular Weight, NMR = ^{13}C NMR spectroscopy, DSC = Differential Scanning Calorimetry, IR = Infra-Red, GC-MS = Gass Chromotography-Mass Spectrometry.

[f] The activities tabulated here have the units gPP/(molZr[propene]h).

[g] Polymerisation performed in the presence of H_2.

Table 7 Ethene polymerisation with cationic Group 4 metallocene catalysts.

Metallocene [a]	Anion [b]	Polymerisation Conditions [c]				Activity/	Analyses[d]	Ref.
		Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ ^{o}C	P/ Bar	$\times 10^{5}$gPP/ (mol M h)$^{-1}$		
1. Metallocenes with two cyclopentadienyl-type ligands								
1.1. $(Cp^1)(Cp^2)MR^+$								
M=Ti, R=Me								
$Cp^1=Cp^2=Cp$	$B(C_6F_5)_4^-$	2.5	50	20	1	5.55	MW, DSC	245
M=Zr, R=Me								
$Cp^1=Cp^2=Cp$	$B(C_6F_5)_4^-$	20	200	25	1	2.1	MW	310
	$MeB(C_6F_5)_3^-$	32	320	25	1	4.5	MW	310
		15	150	25	1	4.00	MW	311
		12.8	320	25	1	45	MW	312
	$B(C_6F_4TBS)_4^-$	10	100	25	1	5.7	MW	310
	$B(C_6F_4TIPS)_4^-$	10	100	25	1	6.2	MW	310
	$MePNB^-$	15	150	23	1	3.7	MW	313
$Cp^1=Cp^2=1,2\text{-}Me_2Cp$	$B(C_6F_5)_4^-$	20	200	25	1	28	MW	310
		20	200	25	1	3.1		310
	$MeB(C_6F_5)_3^-$	20	200	25	1	6.8	MW	310
		15	150	25	1	6.00	MW	311
		8.8	220	25	1	68	MW	312
	$B(C_6F_4TBS)_4^-$	10	100	25	1	1.9	MW	310
	$B(C_6F_4TIPS)_4^-$	10	100	25	1	42	MW	310
	$MePNB^-$	15	150	23	1	8.1	MW	313
$Cp^1=Cp^2=Cp^*$	$B(C_6F_5)_4^-$	20	200	25	1	10	MW	310
	$MeB(C_6F_5)_3^-$	20	200	25	1	3.8	MW	310
		15	150	25	1	3.20	MW	311
		8.8	220	25	1	54	MW	312
	$B(C_6F_4TBS)_4^-$	10	100	25	1	11	MW	310
$Cp^1=Cp^2=1,2\text{-}(SiMe_3)_2Cp$	$MeB(C_6F_5)_3^-$	8.8	220	25	1	38	MW	312
$Cp^1=Cp$, $Cp^2=Cp(C_2H_2NMe_2)$	$B(C_6F_5)_4^-$	2.5	50	20	15	2.33	MW, DSC	245
$Cp^1=\eta^5:\eta^1\text{-}CpMe_4CH_2$, $Cp^2=Cp^*$ [f]	$B(C_6F_5)_4^-$	10	500	-78	1	2.772	MW	314
	$B(C_6F_5)_4^-$	10	500	-50	1	0.466	MW	314
	$B(C_6F_5)_4^-$	10	500	-30	1	0.360	MW	314
	$B(C_6F_5)_4^-$	10	500	-10	1	0.279	MW	314
	$B(C_6F_5)_4^-$	10	500	50	1	0.357	MW	314
	$B(C_6F_5)_4^-$	10	500	60	1	0.259	MW	314
	$B(C_6F_5)_3$	10	500	-70	1	0.970	MW	314
	$B(C_6F_5)_3$	10	500	-50	1	0.784	MW	314
	$B(C_6F_5)_3$	10	500	-20	1	0.400	MW	314
	$B(C_6F_5)_3$	10	500	20	1	0.370	MW	314
	$B(C_6F_5)_3$	5	500	20	1	0.312	MW	
$Cp^1=Cp^2=Cp$, $R=PPh_2Me+\eta^2\text{-}C_2H_4$ [f]	$B(C_6F_5)_3$	(n.g.)	(n.g.).	25	1	0.032	MW	315
	$B(C_6F_5)_3$	(n.g.)	(n.g.).	25	1	0.94	MW	315
$Cp^1=Cp^2=Cp^*$, $R=\eta^4$-butadiene [f]	$B(C_6F_5)_3$	84	420	r.t	1	0.050	NMR, MW, DSC	316
$Cp^1=Cp^*$, $Cp^2=CpMe_4CH_2B(C_6F_5)_3$, $R=C_6F_5$	-	21.1	211	25	1	1.3	MW	257
$Cp^1=Cp^*$, $Cp^2=CpMe_4CH_2B(C_6F_5)_3$, $R=C_6F_5$	-	21.7	217	25	1	1.3	MW	257

Table 7 (cont.)

Metallocene[a]	Anion[b]	Polymerisation Conditions[c]				Activity/	Analyses[d]	Ref.
		Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ ^{o}C	P/ Bar	$\times 10^{5}$gPP/ (mol M h)$^{-1}$		
1.2. Bimetallic Systems[g]								
$(Cp_2ZrMe)_2Me^+$	$MePBB^-$	15	150	25	1	4.80	MW	311
	$MePNB^-$	15	150	23	1	3.4	MW	313
$[(1,2\text{-}Me_2Cp)_2ZrMe]_2Me^+$	$MePBB^-$	15	150	25	1	7.80	MW	311
	$MePNB^-$	15	150	23	1	7.6	MW	313
$[(Cp^*)_2ZrMe]_2Me^+$	$MePBB^-$	15	150	25	1	4.30	MW	311
1.3. $(Ind^1)(Ind^2)MCl_2$								
M=Zr[e]								
Ind^1=Ind^2=tetrahydo-2-MeBenz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	20	15	0.91	NMR, MW, DSC	317
Ind^1=Ind^2=tetrahydo-2,3-Me_2Benz[*f*]Ind	$B(C_6F_5)_4^-$	50	1000	20	15	1.4	NMR, MW, DSC	317
Ind^1=Ind^2=tetrahydo-2,3-Me_2Benz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	20	15	1.3	NMR, MW, DSC	317
Ind^1=Ind^2=tetrahydo-2-Me-3-PhBenz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	20	15	0.36	NMR, MW, DSC	317
1.4. $B(Ind^1)(Ind^2)MX$								
$B=C_2H_4$, M=Zr, $X=\eta^2Me_3SiCCSiMe_3$-[e]								
Ind^1=Ind^2=$IndH_4$	$B(C_6F_5)_3$	6.0	600	r.t.	2	0.125		318
2. Metallocenes with one cyclopentadienyl-type ligand.								
2.1. $(Cp)(NPR_3)TiL$								
$L=Me_2$								
Cp=Cp, R=Cy	$B(C_6F_5)_4^-$	25.1	(n.g.)	25	1	0.231	MW	273
Cp=Cp, R=^{i}Pr	$B(C_6F_5)_4^-$	33.3	(n.g.)	25	1	0.225	MW	273
Cp=Cp, R=^{t}Bu	$B(C_6F_5)_4^-$	21.4	(n.g.)	25	1	0.401	MW	273
Cp=^{t}BuCp, R=Cy	$B(C_6F_5)_4^-$	27.6	(n.g.)	25	1	1.807	MW	273
Cp=^{t}BuCp, R=^{i}Pr	$B(C_6F_5)_4^-$	33.2	(n.g.)	25	1	1.193	MW	273
Cp=^{t}BuCp, R=^{t}Bu	$B(C_6F_5)_4^-$	18.1	(n.g.)	25	1	1.296	MW	273
2.2. (Cp)ML								
M=Ti[f]								
$L=Cl_3$, Cp=Cp[e]	$B(C_6F_5)_4^-$	2.5	50	20	1	0.15	MW, DSC	245
$L=Cl_3$, Cp=Cp^*[e]	$B(C_6F_5)_4^-$	2.5	50	20	1	2.11	MW, DSC	245
$L=Cl_3$, Cp=$Cp(C_2H_4NMe_2)$[e]	$B(C_6F_5)_4^-$	2.5	50	20	1	4.562	MW, DSC	245
$L=Cl_3$ Cp=$Cp(Me_4)(C_2H_4NMe_2)$[e]	$B(C_6F_5)_4^-$	2.5	50	20	1	0.36	MW, DSC	245
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=Cp[e]	$B(C_6F_5)_4^-$	18.	61	60	4	0.077	MW	319
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=Cp^*[e]	$B(C_6F_5)_4^-$	6.5	21.7	60	4	2.220	MW	319
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=^{n}BuCp[e]	$B(C_6F_5)_4^-$	8.6	28.7	60	4	0.302	MW	319
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=^{t}BuCp[e]	$B(C_6F_5)_4^-$	15.	50.3	60	4	0.258	MW	319
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=1,3-Me_2Cp[e]	$B(C_6F_5)_4^-$	24.	80.6	60	4	0.215	MW	319
$L=Cl_2$ + O-2,6-$^{i}Pr_2C_6H_3$, Cp=1,3-$^{t}Bu_2Cp$[e]	$B(C_6F_5)_4^-$	7.2	24.0	60	4	0.653	MW	319
$L=Me_3$, Cp=Cp^*	$B(C_6F_5)_4^-$	60	6000	25	1	0.046		320
$L=Me_3$, Cp=Cp^*	$B(C_6F_5)_3$	60	1714	25	1	0.023		321
$L=Me_3$, Cp=Cp^*	$B(C_6F_5)_4^-$	60	1714	25	1	0.030		321
$L=Me_3$, Cp=$Cp(Me)_4(CH_2)_2Ph$	$B(C_6F_5)_4^-$	2.5	50	50	1	0		275
	$B(C_6F_5)_4^-$	2.5	50	50	1	7.94		275

Table 7 (cont.)

Metallocene[a]	Anion[b]	Polymerisation Conditions[c]				Activity/	Analyses[d]	Ref.
		Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ °C	P/ Bar	$\times 10^5$gPP/ (mol M h)$^{-1}$		
L=Me$_2$+Cl, Cp=Cp*	$B(C_6F_5)_3$	60	1714	25	1	0.016		321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.032		320
	$B(C_6F_5)_4^-$	60	1714	25	1	0.024		321
L=Me$_2$+C$_6$F$_5$, Cp=Cp*	$B(C_6F_5)_3$	60	1714	25	1	0.008		321
	$B(C_6F_5)_4^-$	60	1714	25	1	0.024		321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.016		320
L=Me$_2$+OC$_6$F$_5$, Cp=Cp*	$B(C_6F_5)_3$	60	1714	25	1	0.022		321
	$B(C_6F_5)_4^-$	60	1714	25	1	0.023		321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.044		320
M=Zr[f]								
L=(η^3-C$_3$H$_5$) + (η^4-CH$_2$C(Me)C(Me)CH$_2$), Cp=1,3-(SiMe$_3$)$_2$Cp	$B(C_6F_5)_3$	25	1250	0	1	98.7	MW	322
		25	1250	20	1	63.3	MW	322
		25	1250	44	1	43.2	MW	322
		25	1250	60	1	45.6	MW	322
2.3. Bimetallic Systems								
[Cp(CpC$_2$H$_4$NMe$_2$.HCl)TiCl]$_2$O	$B(C_6F_5)_4^-$	2.5	50	20	1	0.70	MW, DSC	245
(μ-C$_{12}$H$_8${[SiPh(Ind)$_2$}ZrCl$_2$}$_2$	$B(C_6F_5)_4^-$	(n.g.)	1.0	40	1	19.9	NMR, MW, DSC	262
	$B(C_6F_5)_4^-$	(n.g.)	1.0	60	1	21.5	NMR, MW, DSC	262
	$B(C_6F_5)_4^-$	(n.g.)	1.0	80	1	60.0	NMR, MW, DSC	262
	$B(C_6F_5)_4^-$	(n.g.)	1.0	10	1	18.2	NMR, MW, DSC	262
2.4. Constrained Geometry Catalysts								
η^5:η^1-CpSiMe$_2$(NR)MR$_2^+$[f]								
Cp=Me$_4$Cp, R=^{t}Bu, M=Ti, R$_2$=Me	$B(C_6F_5)_3$	15	300	25	1	0.114	MW, DSC	323
	$B(C_6F_5)_3$	15	150	25	1	0.084	MW	311
	$B(C_6F_5)_4^-$	15	300	25	1	0.124	MW, DSC	323
	PBB	15	150	25	1	4.98	MW	311
	PNB	15	150	23	1	0.29	MW	313
Cp=Me$_4$Cp, R=^{t}Bu, M=Ti, R$_2$=Bz	$B(C_6F_5)_3$	15	300	25	1	0.200	MW, DSC	323
	$B(C_6F_5)_4^-$	15	300	25	1	0.156	MW, DSC	323
Cp=TCP, M=Ti, R$_2$=Bz	$B(C_6F_5)_3$	15	150	25	1	0.014	MW, DSC	324
	$B(C_6F_5)_4^-$	15	150	25	1	0.021	MW, DSC	324
Cp=Me$_4$Cp, R= ^{t}Bu, M=Zr, R$_2$=Me	$B(C_6F_5)_4^-$	0.2		25	1	0.91	MW	310
	$B(C_6F_5)_3$	0.4		25	1	<0.001		310
	$B(C_6F_5)_3$	15	150	25	1	0		311
	$B(C_6F_4TBS)_4^-$	0.2		25	1	0.052	MW	310
	$B(C_6F_4TIPS)_4^-$	0.2		25	1	0.060	MW	310
	PBB	15	150	25	1	1.56	MW	311
	PNB	15	150	23	1	0.0037	MW	313
3. ML^{1}L^2								
M=Ti, L^1=Cl$_2$[f]								
L^2=(^{t}Bu$_3$PN)$_2$	$B(C_6F_5)_3$	(n.g.)	12100	25	1	0.167		325
	$B(C_6F_5)_4^-$	(n.g.)	21500	25	1	1.166		325
	$B(C_6F_5)_3$	(n.g.)	13.89	160	103	3.060	MW	325
	$B(C_6F_5)_4^-$	(n.g.)	13.89	160	103	3.250		325
	$B(C_6F_5)_4^-$	(n.g.)	0.58	160	103	62.31	MW	325

Table 7 (cont.)

Metallocene [a]	Anion [b]	Polymerisation Conditions [c]				Activity/	Analyses[d]	Ref.
		Mol M/ $\times10^{-6}$mol	[M]/ $\times10^{-6}$M	T/ ^{o}C	P/ Bar	$\times10^5$gPP/ (mol M h)$^{-1}$		
M=Zr, L^1=$(Me)_2$-[f]								
L^2=(2,6-$_2C_6H_3$)MeSiNCH$_2$CH$_2$NSiMe(2,6-Me$_2C_6H_3$)	$B(C_6F_5)_4^-$	(n.g.)	(n.g.).	50	10	0.60		293
L^2=N(Si^{i}Pr$_3$)(2-C_6H_4-CH$_2$CH$_2$-2-C_6H_4)(Si^{i}Pr$_3$)N	$B(C_6F_3)$	7.7	777	0	1	0.178	MW	292

[a] Many of the metallocenes included in this table are shown as polymerisation active, 14-electron cationic species. The exceptions are those where the cationic species in generated *in situ* or where the cationic species bears little resemblance to its parent. These have been indicated as such (*vide infra*).

[b] The weakly co-ordinating anion generated from the catalyst activation step.

[c, d] The explanation for the terms in this section of the table may be found as footnotes to Tables 5 and 6.

[e] Cationic species generated *in situ* employing TIBA.

[f] For clarity the unactivated metallocene is shown here.

[g] These bimetallic catalysts are generated from their monomeric parents after activation by the co-catalyst.

Table 8 Propene polymerisation with cationic Group 4 metallocene catalysts.

Metallocene [a]	Anion [b]	Polymerisation Conditions [c] Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ °C	P/ Bar	Activity/ $\times 10^{5}$gPP/ (mol M h)$^{-1}$	Analyses[d]	Ref.
1. Metallocenes with two cyclopentadienyl-type ligands								
1.1. $(Cp^1)(Cp^2)MR^+$								
M=Ti, R=Me								
$Cp^1=Cp^2=Cp$	$B(C_6F_5)_4^-$	5.0	100	20	1.4	2.34	MW	245
M=Zr, R=Me								
$Cp^1=Cp^2=Cp$	$B(C_6F_5)_4^-$	0.39	3900	25	1	10.8	MW	310
	$MeB(C_6F_5)_3^-$	0.49	4900	25	1	8.1		310
	$B(C_6F_4TBS)_4^-$	0.38	3800	25	1	7.5	MW	310
	$B(C_6F_4TIPS)_4^-$	0.38	3800	25	1	9.0	MW	310
$Cp^1=Cp^2$ =1,2-Me_2Cp	$B(C_6F_5)_4^-$	0.39	3900	25	1	10.2	MW	310
	$MeB(C_6F_5)_3^-$	0.49	4900	25	1	2.8		310
	$B(C_6F_4TBS)_4^-$	0.37	3700	25	1	0.37	MW	310
	$B(C_6F_4TIPS)_4^-$	0.33	3300	25	1	0.33	MW	310
$Cp^1=Cp^2=Cp^*$	$B(C_6F_5)_4^-$	0.39	3900	25	1	1.3	MW	310
	$MeB(C_6F_5)_3^-$	0.49	4900	25	1	2.3		310
	$B(C_6F_4TBS)_4^-$	0.35	3500	25	1	1.3	MW	310
	$B(C_6F_4TIPS)_4^-$	0.31	3100	25	1	1.2	MW	310
$Cp^1=Cp$, $Cp^2=C_2H_2NMe_2$	$B(C_6F_5)_4^-$	5.0	100	20	1.4	0		245
M=Zr, R=η^4-butadiene [f]								
$Cp^1=Cp^2=Cp^*$	$B(C_6F_5)_3$	84	420	-20	2	0.18	NMR, MW	316
	$B(C_6F_5)_3$	84	420	0	2	0.60	NMR, MW	316
	$B(C_6F_5)_3$	84	420	20	2	0.50	NMR, MW	316
1.2. $(Ind^1)(Ind^2)MCl_2$								
M=Zr [e]								
$Ind^1=Ind^2$=tetrahydo-2-MeBenz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	0	15	0.31	NMR, MW, DSC	317
	$B(C_6F_5)_4^-$	50	1000	-20	15	0.38	NMR, MW, DSC	317
$Ind^1=Ind^2$=tetrahydo-2,3-Me_2Benz[*f*]Ind	$B(C_6F_5)_4^-$	50	1000	0	15	0.66	NMR, MW, DSC	317
	$B(C_6F_5)_4^-$	50	1000	-20	15	0.78	NMR, MW, DSC	317
$Ind^1=Ind^2$=tetrahydo-2,3-Me_2Benz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	0	15	0.34	NMR, MW, DSC	317
	$B(C_6F_5)_4^-$	50	1000	-20	15	1.50	NMR, MW, DSC	317
$Ind^1=Ind^2$=tetrahydo-2-Me-3-PhBenz[*e*]Ind	$B(C_6F_5)_4^-$	50	1000	0	15	0.052	NMR, MW, DSC	317
	$B(C_6F_5)_4^-$	50	1000	-20	15	0.076	NMR, MW, DSC	317
1.3. $B(Ind^1)(Ind^2)MX$								
M=Zr, X=Cl_2 , B=CR^1CR^2 [e]								
$CR^1CR^2=C_2H_4$, $Ind^1=Ind^2$=Ind	$B(C_6F_5)_4^-$	5	100	-20	2.0	4.60	NMR, MW, DSC	261
	$B(C_6F_5)_4^-$	0.5	10	0	1	17.2	DSC	326
$CR^1CR^2=C_2H_4$, $Ind^1=Ind^2$=2-[$OSi(Me)_2{}^tBu$]Ind	$B(C_6F_5)_4^-$	5	100	-20	2.0	7.50	NMR, MW, DSC	261
M=Zr, X=Cl_2 , B=$SiMe_2$ [e]								
$Ind^1=Ind^2$=Ind	$B(C_6F_5)_3$	5	100	-20	2.0	4.60	NMR, MW, DSC	261

Table 8 (cont.)

Metallocene[a]	Anion[b]	Polymerisation Conditions[c]				Activity/	Analyses[d]	Ref.
		Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ °C	P/ Bar	$\times 10^5$gPP/ (mol M h)$^{-1}$		
M=Zr, X=Cl_2, B=-$SiMe_2$-O-Me_2Si-[e]								
$Ind^1=Ind^2=Ind$	$B(C_6F_5)_4^-$	2.5	50	-50	1.03	2.88	MW, DSC	263
	$B(C_6F_5)_4^-$	2.5	50	-20	1.03	3.60	MW, DSC	263
	$B(C_6F_5)_4^-$	2.5	50	0	1.03	1.08	MW, DSC	263
	$B(C_6F_5)_4^-$	2.5	50	20	1.03	1.20	MW, DSC	263
M=Zr, X=Me								
$Ind^1=Ind^2=Ind$	$MePNB^-$	10	200	24	1	21	NMR, MW	313
	$MePNB^-$	10	200	60	1	32	NMR, MW	313
M=Zr, B= GeR[e]								
$Ind^1=Ind^2=Ind$,	$B(C_6F_5)_4^-$	0.5	50	-60	0.69	99.6	MW, DSC	169
R=1,2,3,4-Ph_4-1,3-butadiene-1,4-diyl		0.5	50	-40	0.69	144	MW, DSC	169
		0.5	50	-20	0.69	126	MW, DSC	169
		0.5	50	0	0.69	110	MW, DSC	169
		0.5	50	25	0.69	46	MW, DSC	169
2. Metallocenes with one Cyclopentadienyl-type ligand								
2.1. CpML[f]								
M=Ti								
L=Cl_3, Cp=Cp[e]	$B(C_6F_5)_4^-$	5.0	100	20	1.4	0		245
L=Cl_3, Cp=Cp^*[e]	$B(C_6F_5)_4^-$	5.0	100	20	1.4	0.59	MW	245
L=Cl_3, Cp=Cp($C_2H_4NMe_2$)[e]	$B(C_6F_5)_4^-$	5.0	100	20	1.4	0.752	MW	245
L=Cl_3, Cp=Cp(Me_4)($C_2H_4NMe_2$)[e]	$B(C_6F_5)_4^-$	5.0	100	20	1.4	0		245
L=Me_3, Cp=Cp^*	$B(C_6F_5)_4^-$	60	6000	-78	1	0.43	NMR, MW	245
	$B(C_6F_5)_4^-$	60	6000	0	1	2.14	NMR, MW	245
	$B(C_6F_5)_4^-$	60	6000	25	1	1.22	NMR, MW	245
	$B(C_6F_5)_4^-$	60	1714	25	1	0.225	MW	321
	$B(C_6F_5)_3$	60	1714	25	1	0.077	MW	321
L=Me_3, Cp=Cp(CMe_2CH_2Ph)	$B(C_6F_5)_4^-$	40	(n.g.)	0	1	0.64[g]	MW	327
		40	(n.g.)	20	1	1.62[g]	MW	327
		40	(n.g.)	40	1	1.88[g]	MW	327
		40	(n.g.)	60	1	1.60[g]	MW	327
L=Me_3, Cp=Cp($SiMe_2Ph$)	$B(C_6F_5)_4^-$	20	(n.g.)	0	1	7.6[g]	MW	327
		20	(n.g.)	-20	1	3.3[g]	MW	327
L=Bz_3, Cp=Cp(CPh_2)	$B(C_6F_5)_4^-$	20	(n.g.)	0	1	0.35[g]	MW	327
		20	(n.g.)	-20	1	4.76[g]	MW	327
L=Me_2 + Cl, Cp=Cp^*	$B(C_6F_5)_4^-$	60	6000	-78	1	0.43	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	0	1	1.19	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.79	NMR, MW	321
	$B(C_6F_5)_4^-$	60	1714	25	1	0.246	MW	321
	$B(C_6F_5)_3$	60	1714	25	1	0.029	MW	321
	$B(C_6F_5)_3$	40	2000	70	1	0.20	MW	96
	$B(C_6F_5)_3$	40	2000	40	1	0.14	MW	96
	$B(C_6F_5)_3$	20	333	0	1	4.098	MW	96
	$B(C_6F_5)_3$	20	333	-20	1	8.070	MW	96
	$B(C_6F_5)_3$	20	200	-45	l.p.	5.2	MW	96
L=Me_2+C_6F_5, Cp=Cp^*	$B(C_6F_5)_4^-$	60	6000	-78	1	0.22	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	0	1	1.56	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.74	NMR, MW	321
	$B(C_6F_5)_4^-$	60	1714	25	1	0.222	MW	321
	$B(C_6F_5)_3$	60	1714	25	1	0.078	MW	321

Table 8 (cont.)

Metallocene [a]	Anion [b]	Polymerisation Conditions [c]				Activity/	Analyses [d]	Ref.
		Mol M/ $\times 10^{-6}$mol	[M]/ $\times 10^{-6}$M	T/ °C	P/ Bar	$\times 10^{5}$gPP/ (mol M h)$^{-1}$		
L=Me_2+OC_6F_5, Cp=Cp*	$B(C_6F_5)_4^-$	60	6000	-78	1	0.33	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	0	1	1.55	NMR, MW	321
	$B(C_6F_5)_4^-$	60	6000	25	1	0.94	NMR, MW	321
	$B(C_6F_5)_4^-$	60	1714	25	1	0.174	MW	321
	$B(C_6F_5)_3$	60	1714	25	1	0.160	MW	321
L=Bz_2, Cp=[Cp(Me_4)($CH_2CH_2CH_2O$)]	$B(C_6F_5)_3$	(n.g.)	(n.g.)	r.t.	4	2.63	NMR, MW	328
2.2. η^5:η^1-CpSiMe_2(NR)MR_2 [f]								
Cp=Me_4Cp, R=^{t}Bu, M=Zr, R_2=Me	$B(C_6F_5)_4^-$	290	2900	25	1	8.2	MW	310
	$MeB(C_6F_5)_3^-$	470	4700	25	1	0		310
	$B(C_6F_4TBS)^-$	35000	350000	25	1	0.16	MW	310
	$B(C_6F_4TIPS)_4^-$	63000	630000	25	1	0.16	MW	310
Cp=Me_4Cp, R=^{t}Bu, M=Ti, R_2=Bz	$B(C_6F_5)_3$	15	300	25	1	1.69	NMR, MW	323
	$B(C_6F_5)_4^-$	15	300	25	1	21.2	NMR, MW	323
Cp=TCP, M=Ti, R_2=Bz	$B(C_6F_5)_4^-$	20	400	25	1	0.382	NMR, MW, DSC	324
2.3. η^5:η^1-9-FluSiMe_2(NR)ML [f]								
M=Ti								
Flu=Flu, R=^{t}Bu, L=Me_2	$B(C_6F_5)_4^-$	40	1333	-50	1	0.016	NMR, MW	329
	$B(C_6F_5)_4^-$	40	1333	40	1	0.088	NMR, MW	330
	$B(C_6F_5)_3^-$	40	1333	-50	1	0.005	NMR, MW	329
	$B(C_6F_5)_3$	40	1333	40	1	0.10	NMR, MW	330
3. M$L^1$$L^2$								
M=Zr, L^1=Me_2								
L^2=N(Si^iPr_3)(2-C_6H_4-CH_2CH_2-2-C_6H_4)(Si^iPr_3)N	$B(C_6F_5)_3$	7.77	777	0	1	2.85	MW	292
M=Zr, L^1=Bz_2								
L^2=($C_{10}H_6CH_2$)$_2$NMe	$B(C_6F_5)_4^-$	(n.g.)	(n.g.)	r.t.	4	0.26	MW	331

[a] Many of the metallocenes included in this table are shown as polymerisation active, 14-electron cationic species. The exceptions are those where the cationic species in generated *in situ* or where the cationic species bears little resemblance to its parent. These have been indicated as such (*vide infra*).

[b] The weakly co-ordinating anion generated from the catalyst activation step.

[c, d] The explanation for the terms in this section of the table may be found in the footnotes to Tables 5 and 6.

[e] Cationic species generated *in situ* employing TIBA.

[f] For clarity the unactivated metallocene is shown here.

[g] Units for activity are gPP(molTi)$^{-1}$[C_3H_6]$^{-1}$h^{-1}bar^{-1}.

Table 9 Co-polymerisation reactions involving Group 4 metallocenes.

Monomers	Catalysts	Polymer Analysis	Ref.
iso-Butene, Isoprene	$Cp_2TiMe_2/B(C_6F_5)_3$	NMR, MW	332
	$Cp_2ZrMe_2/B(C_6F_5)_3$	MW	333
Butadiene, Styrene	**$M(OCOR)_2$**		
	M=Nd		
	$R=CH_3$	NMR, MW, IR	334
	$R=CF_3$	NMR, MW, IR	334
	$R=CCl_3$	NMR, MW, IR	334
	$R=CH_2Cl$	NMR, MW, IR	334
Ethene, 1-Butene	$Me_2Si(Ind)_2ZrCl_2/MAO$	NMR, MW, DSC	335
Ethene, 1-Dodecene	$Me_2C(Cp)(Flu)ZrCl_2/MAO$	NMR	336
	$Me_2Si(Ind)_2ZrCl_2/MAO$	NMR	336
Ethene, 1-Hexene	$Et[2\text{-}(OSiMe_2{}^tBu)Ind]_2ZrCl_2$	NMR, MW, DSC	261
	$Cp^*TiMe_3/B(C_6F_5)_3$	MW	311
	Cp^*TiMe_3/PBB	MW	311
	η^5: η^1-$CpSiMe_2(NR)MR_2/X$		
	M=Ti, X=$B(C_6F_5)_3$		
	Cp=$CpMe_4$, R=^{t}Bu, R_2=Me	MW	311
	M=Ti, X=PBB		
	Cp=$CpMe_4$, R=^{t}Bu, R_2=Me	MW	311
	M=Ti, X=PNB		
	Cp=$CpMe_4$, R=^{t}Bu, R_2=Me	MW	313
	M=Zr, X=$B(C_6F_5)_3$		
	Cp=$CpMe_4$, R=^{t}Bu, R_2=Me	MW	311
	M=Zr, X=PBB		
	Cp=$CpMe_4$, R=^{t}Bu, R_2=Me	MW	311
Ethene, Norbornene	$[MeHC(Cp)_2]ZrCl_2/MAO$		337
	$[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2/MAO$		337
	$[Me_2C(3\text{-}{}^iPrCp)(Flu)]ZrCl_2/MAO$		337
	$[Me_2C(3\text{-}{}^tBuCp)(Flu)]ZrCl_2/MAO$	NMR, MW, DSC	338, 337
	$[Me_2C(Cp)(Ind)]ZrCl_2/MAO$		339
	$[Me_2C(3\text{-}MeCp)(Ind)]ZrCl_2/MAO$		337
	$[Me_2C(3\text{-}{}^tBuCp)(Ind)]ZrCl_2/MAO$		337
	$[Me_2Si(3\text{-}{}^tBuCp)(Flu)]ZrCl_2/MAO$		337

Table 9 (cont.)

Monomers	Catalysts	Polymer Analysis	Ref.
	η^5: η^1-(CpR)SiMe$_2$(NR)ML$_2$/MAO		
	M=Ti, CpR=CpMe$_4$, R=^{t}Bu, L=Cl		337
	M=Ti, CpR=CpMe$_4$, R=^{t}Bu, L=Cl	NMR, MW, DSC	340
	M=Zr, CpR=CpMe$_4$. R=^{t}Bu, L=Cl		337
	M=Ti, CpR=3-^{t}BuCp, R=^{t}Bu, L=Me	NMR, MW, DSC	340
	M=Zr, CpR=3-^{t}BuCp, R=adamantyl, L=Me	NMR, MW, DSC	341
	M=Hf, CpR=3-^{t}BuCp, R=adamantyl, L=Me	NMR, MW, DSC	341
	η^5: η^1-(Ind)SiMe$_2$(NR)ML$_2$/MAO		
	M=Ti, Ind=Ind, R=^{t}Bu, L=Cl	NMR, MW, DSC	340
	η^5: η^1-(9-Flu)SiMe$_2$(NR)MCl$_2$/MAO		
	M=Zr, R=^{t}Bu		337
Ethene, 1-Octadecene	Me$_2$C(Cp)(Flu)ZrCl$_2$/MAO	NMR	336
	Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO	NMR	336
Ethene, 1-Octene	Cp$_2$ZrCl$_2$/MAO	NMR, MW, DSC	335
	B(Ind^1)(Ind^2)MCl$_2$/MAO		
	M=Zr, B=-SiMe$_2$		
	Ind^1=Ind^2=Ind	NMR, MW, DSC	342
	Ind^1=Ind^2=2-MeInd	NMR, MW, DSC	342
	Ind^1=Ind^2=Benz[e]Ind	NMR, MW, DSC	342
	Ind^1=Ind^2=2-MeBenz[e]Ind	NMR, MW, DSC	342
	η^5: η^1-(CpMe$_4$)SiMe2(N^{t}Bu)TiMe$_2^+$/ B(C$_6$F$_5$)$_3$		313
	η^5:η^1-2-MeBenz[e]IndSiMe$_2$(N^{t}Bu)TiCl$_2$/MAO		343
	B(1-NR$_2$-BC$_5$H$_4$)$_2$MCl$_2$		
	M=Zr		
	B=C$_2$H$_4$, R=^{i}Pr	MW	344
	B=-SiMe$_2$, R=^{i}Pr	MW	344
	B=-CMe$_2$, R=^{i}Pr	MW	344

Table 9 (cont.)

Monomers	Catalysts	Polymer Analysis	Ref.
Ethene, Propene	Cp_2ZrCl_2/MAO	NMR, MW	249
	$Me_2C[3\text{-}^tBu\text{-}Cp]_2ZrCl_2$/MAO	NMR, η	345
	$[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO	NMR, MW, DSC	346
	$[Me_2C(3\text{-}^iPrCp)(Flu)]ZrCl_2$/MAO	NMR, MW, DSC	346
	$[Me_2C(3\text{-}^tBuCp)(Flu)]ZrCl_2$/MAO	NMR, MW, DSC	346
	$[2\text{-}PhInd]_2ZrCl_2$/MAO	NMR, MW	133
	$Me_2C[3\text{-}^tBu\text{-}Ind]_2ZrCl_2$/MAO	NMR, η	345
	$[2\text{-}(3,5\text{-}CF_3Ph)Ind]_2ZrCl_2$/MAO	NMR, MW	133
	$Et[4,7\text{-}Me_2\text{-}Ind]_2ZrCl_2$/MAO	NMR, η	345
	$Et[4,7\text{-}Me_2\text{-}IndH_4]_2ZrCl_2$/MAO	NMR, η	345
	$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$/MAO	NMR, η	345
	$(TP)(Cp)ZrCl_2$/MAO	NMR, MW	249
	$B(Ind^1)(Ind^2)MCl_2$/MAO		
	M=Zr, $B=CH_2CH_2$		
	$Ind^1=Ind^2=Ind$	NMR, MW	133
	$Ind^1=Ind^2=Ind$	NMR, DSC	347
	M=Zr, $B=\text{-}SiMe_2$		
	$Ind^1=Ind^2=Ind$	NMR, MW, DSC	335
	$Ind^1=Ind^2=2\text{-}MeInd$	NMR, MW, DSC	335
	$Ind^1=Ind^2=Benz[e]Ind$	NMR, MW, DSC	335
	$Ind^1=Ind^2=2\text{-}MeBenz[e]Ind$	NMR, MW, DSC	335, 348
	$CpTiCl_3$/MAO	NMR, DSC	347
	$CpTi(OBz)_3$/MAO	NMR, MW, DSC	349
	$CpTi(OPh_3)_3$/MAO	NMR, MW, DSC	350
	$(TP)ZrCl_3$/MAO	NMR, MW	249
	$(TP^*)Zr(O^tBu)_3$/MAO	MW	249
	η^5: η^1-$CpSiMe_2(NR)TiCl_2$/MAO		
	$R=^tBu$		335
	$R=^tBu$	NMR, MW, DSC	351
	R=Bz	NMR, MW, DSC	351
	η^5: η^1-$(1\text{-}Ind)SiMe_2(NR)TiCl_2$/MAO		
	1-Ind=Ind, $R=^tBu$	NMR, MW, DSC	351
	1-Ind=3-$(SiMe_3)$Ind, $R=^tBu$	NMR, MW, DSC	351
	η^5: η^1-$(9\text{-}Flu)SiMe_2(NR)TiCl_2$/X		
	Flu=Flu, $R=^tBu$, X=MAO	NMR, MW, DSC	351, 352
	Flu=Flu, $R=^tBu$, $X=B(C_6F_5)_4$	NMR, MW, DSC	352

Table 9 (cont.)

Monomers	Catalysts	Polymer Analysis	Ref.
Ethene, 10-Undecen-1-ol	Ind_2ZrCl_2	NMR, MW, DSC	353
	$Et[Ind]_2ZrCl_2$	NMR, MW, DSC	353
	$Me_2Si[Ind]_2ZrCl_2$	NMR, MW, DSC	353
	$Me_2Si[2\text{-}MeInd]_2ZrCl_2$	NMR, MW, DSC	353
	$Me_2Si[2\text{-}MeBenz(e)Ind]_2ZrCl_2$	NMR, MW, DSC	353
Ethene, 5-Vinyl-2-Norbornene	Cp_2ZrCl_2/MAO	NMR, IR	354
Ethene, 6-^{t}Butyl-2-(1,1-dimethyl	$Me_2Si(IndH_4)_2ZrCl_2$/MAO	NMR, MW, DSC, UV	355
hept-6-enyl)-4-methylphenol	$Et(IndH_4)_2ZrCl_2$/MAO	NMR, MW, DSC, UV	355
	Cp_2ZrCl_2/MAO	NMR, MW, DSC, UV	355
1,5-Hexadiene, 1,7-Octadiene	$Me_2Si(Ind)_2ZrCl_2$	NMR, MW, DSC	356
	$Ph_2C(Cp)(Flu)ZrCl_2$	NMR, MW, DSC	356
Propene, 10-Undecen-1-ol	Ind_2ZrCl_2	NMR, MW, DSC	353
	$Me_2Si[Ind]_2ZrCl_2$	NMR, MW, DSC	353
	$Me_2Si[2\text{-}MeInd]_2ZrCl_2$	NMR, MW, DSC	353
	$Me_2Si[2\text{-}MeBenz(e)Ind]_2ZrCl_2$	NMR, MW, DSC	353
Styrene, (Z)-1,3-Pentadiene	$CpTiCl_3$/MAO	NMR, MW	357

Table 10 Polymerisation of other olefin molecules by Group 4 metallocene catalysts.

Monomer	Catalyst	Polymer Analysis	Ref.
iso-Butene	$Cp_2TiMe_2/B(C_6F_5)_3$	NMR, MW	332
	$Cp_2ZrMe_2/B(C_6F_5)_3$	MW	333
	$Cp_2ZrMe_2/B(C_6F_5)_4$		358
	$[Cp_2ZrH_2]_2/B(C_6F_5)_3$		358
Cyclopentene	$Et(Ind)ZrCl_2/MAO$	NMR, GC-MS	359
		NMR, XRD	360
Decene	**$[R^1NC_3H_6NR^1]MX_2/MAO$**		
	M=Ti		
	$R^1=2,6-{}^iPr_2-C_6H_3$ $X_2=Me$	MW	361
	$R^1=2,6-Me_2-C_6H_3$ $X_2=Me$	MW	361
1,5-Hexadiene	$(Cp^*)TiMe3/B(C_6F_5)_3$	NMR, MW	362
Hexene	$Me_2Si(Cp)(3,4-Me_2Cp)ZrCl_2/MAO$	MW	363
	$CpTiMe_2/$ $X=B(C_6F_5)_4$	NMR, MW	364
	$Cp^*ZrMe_2[NCyC(Me)NCy]$	NMR, MW	365
	$Cp^*ZrMe_2[NCyC(Me)NEt]$	NMR, MW	365
	$[R^1NC_3H_6NR^1]MX_2/MAO$		
	M=Ti		
	$R^1=2,6-{}^iPr_2-C_6H_3$ $X_2=Cl$	MW	366,361
	$R^1=2,6-Me_2-C_6H_3$ $X_2=Cl$	MW	366,361
	$R^1=2,6-{}^iPr_2-C_6H_3$ $X_2=Me$	MW	366,361
	$R^1=2,6-Me_2-C_6H_3$ $X_2=Me$	MW	366,361
	ML^1L^2/X		
	M=Ti, X=MAO		
	$L^1=RN(CH_2)_3NR$, $L^2=Me_2$		
	$R=2,6-{}^iPr_2C_6H_3$	MW	367
	$R=2,6-Me_2C_6H_3$	MW	367
	M=Ti, $X=B(C_6F_5)_3$		
	$L^1=RN(CH_2)_3NR$, $L^2=Me_2$		
	$R=2,6-{}^iPr_2C_6H_3$	MW	367
	$R=2,6-Me_2C_6H_3$	MW	367
	M=Ti, $X=B(C_6F_5)_4$		
	$L^1=RN(CH_2)_3NR$, $L^2=Me_2$		
	$R=2,6-{}^iPr_2C_6H_3$	MW	367
	$R=2,6-Me_2C_6H_3$	MW	367

Table 10 (cont.)

Monomer	Catalyst	Polymer Analysis	Ref.
	M=Zr, X=MAO		
	$L^1=Cl_2$, $L^2=N(Si^iPr_3)(2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}2\text{-}C_6H_4)\text{-}(Si^iPr_3)N$	MW	292
	$L^1=Me_2$, $L^2=N(Si^iPr_3)(2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}2\text{-}C_6H_4)\text{-}(Si^iPr_3)N$	MW	292
	M=Zr, X=$B(C_6F_5)_3$		
	$L^1=Me_2$, $L^2=N(Si^iPr_3)(2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}2\text{-}C_6H_4)\text{-}(Si^iPr_3)N$	MW	292
3-Methyl-1-butene	$(Ind)_2ZrCl_2$/MAO	DSC	98
	(Benz[*e*]Ind)$_2$ZrCl$_2$/MAO	DSC	98
Methyl Methacrylate	Cp_2ZrMe_2/MAO	MW	368
	Cp_2ZrMe_2/MAO	NMR, MW	369
	$(Cp)(Cp^*)ZrMe_2$/MAO	NMR, MW	369
	$(Cp)(Flu)ZrMe_2$/MAO	NMR, MW	369
	$(Ind)_2ZrMe_2$/MAO	NMR, MW	369
	$[Cp_2ZrMe(THF)][BPh_4]$	MW	368
	$C_2H_4(Ind)_2ZrMe_2/B(C_6F_5)_4$	NMR, MW	370
	$C_2H_4(IndH_4)_2ZrMe_2/B(C_6F_5)_4$	NMR, MW	370
	$Me_2Si(Ind)_2ZrMe_2/B(C_6F_5)_4$	NMR, MW	370
3-Methyl-1-pentene	$(Ind)_2ZrCl_2$/MAO	DSC	98
	(Benz[*e*]Ind)$_2$ZrCl$_2$/MAO	DSC	98
3-Methyl-1,3-pentadiene	$CpTiCl_3$/MAO	NMR	371
Norbornene	$Cp^*TiCl_3/B(C_6F_5)_3$	NMR, MW	362
Octene	$[R^1NC_3H_6NR^1]TiX_2$/MAO		
	$R^1=2,6\text{-}{}^iPr_2\text{-}C_6H_3$ $X_2=Me$	MW	361
	$R^1=2,6\text{-}Me_2\text{-}C_6H_3$ $X_2=Me$	MW	361
Styrene	**B(Cp)(Ind)MCl$_2$**		
	M=Ti, B=-CPh_2		155
	M=Zr, B=-CMe_2		155
	M=Zr, B=-CPh_2		155
	M=Hf, B=-CPh_2		155

Table 10 (cont.)

Monomer	Catalyst	Polymer Analysis	Ref.
Styrene (cont.)	**(Cp)ML/X**		
	M=Ti, X=MAO		
	Cp=Cp		274
	Cp=Cp*, L=Cl_3		245
	Cp=Cp*, L=Cl_3	MW	95
	Cp=Cp*, L=$(Me)_3$	MW	372
	Cp=Cp*, L=$(Me)_3$	NMR, MW	249
	Cp= Cp*, L=$(Bz)_3$	MW	372
	Cp=$Cp(CH_2)_2Ph$, L=Cl_3		277
	Cp=$Cp(Me_4)(CH_2CH_2Ph)$, L=Cl_3	DSC	275
	Cp=$CpMe_4C_2H_4NMe_2$, L=Cl_3		245
	Cp=$CpCH_2$-2-C_5H_4N, L=$(O^iPr)_3$		277
	Cp=$CpMe_4SiMe_2NCH_2CH_2Si(OCH_3)_3$, L=$[N(Et)_2]_2$	MW, DSC	281
	Cp=Cyclopenta[*l*]phenanthryl	MW	95
	Cp=2-MeCyclopenta[*l*]phenanthryl	MW	95
	Cp=2-PhCyclopenta[*l*]phenanthryl	MW	95
	M=Ti, X=$B(C_6F_5)_3$		
	Cp= Cp*, L=$(Me)_3$	MW	372
	Cp= Cp*, L=$(Bz)_3$	MW	372
	M=Ti, X=$B(C_6F_5)_4$		
	Cp= Cp*, L=$(Me)_3$	MW	372
	Cp= Cp*, L=$(Bz)_3$	MW	372
	Cp=$Cp(Me_4)(CH_2CH_2Ph)$, L=Me_3		275
	Cp=TCP, L=$(Bz)_3$	MW	324
	M=Ti, X=PBB		
	CpR= Cp*, L=$(Me)_3$	MW	311
	M=Zr, X=PBB		
	CpR= Cp*, L=$(Me)_3$	MW	311
	M=Hf, X=PBB		
	CpR= Cp*, L=$(Me)_3$	MW	311
	(Ind)MX		
	M=Ti, X=Cl_3		
	Ind=Ind		373
	Ind=1-MeInd		374
	Ind=1-EtInd		374
	Ind=1-^{i}PrInd		374
	Ind=1=$(SiMe_3)$Ind		374
	Ind=1,2-Me_2Ind		374
	Ind=2-(O-$SiMe_3$)Ind		375

Table 10 (cont.)

Monomer	Catalyst	Polymer Analysis	Ref.
Styrene (cont.)	Ind=1-PhInd		376
	Ind=1,3-Ph_2Ind		376
	Ind=1-BzInd		376
	Ind=1-[$(CH_2)_2$Ph]Ind		376
	Ind=Benz[*e*]indenyl		376
	Ind=2-MeBenz[*e*]indenyl		376
	Ind=1,2,3-Me_3Benz[*e*]indenyl		376
	$(C_2B_9)H_{11}ML^1L^2/X$		
	M=Ti, X=MAO		
	$L^1=(NEt_2)_2$, $L^2=NHEt_2$		274
	M=Zr, X=MAO		
	$L^1=(NEt_2)_2$, $L^2=NHEt_2$		274
	M=Ti, X=TIBA		
	$L^1=(NEt_2)_2$, $L^2=NHEt_2$		274
	M=Zr, X=TIBA		
	$L^1=(NEt_2)_2$, $L^2=NHEt_2$		274
	(TP)MCl_3 /MAO		
	M=Ti	NMR, MW	249
	M=Zr	NMR, MW	249
	[2,2'-R^1(4-R^2-6-$R^3C_6H_2$-O$)_2$]MX_2		
	M=Ti		
	$R^1=CH_2$, R^2=Me, $R^3=CMe_3$, X=Cl	MW, DSC	377
	$R^1=CH_2CH_2$, R^2=Me, $R^3=CMe_3$, X=Cl	MW, DSC	377
	$R^1=CH_2CH_2$, R^2=Me, $R^3=CMe_3$, X=Cl+ Cp^*	MW, DSC	377
	$R^1=CH_2CH_2$, R^2=Me, $R^3=CMe_3$, X=O^iPr	MW, DSC	377
	R^1=S, R^2=Me, $R^3=CMe_3$, X=Cl+ Cp^*	MW, DSC	377
	R^1=S, R^2=Me, $R^3=CMe_3$, X=Cl	MW, DSC	377
	R^1=S, R^2=Me, $R^3=CMe_3$, X=O^iPr	MW, DSC	377
	R^1=S, R^2=Me, $R^3=CMe_3$, X=Cl+O^iPr	MW, DSC	377
	R^1=SO, R^2=Me, $R^3=CMe_3$, X=Cl	MW, DSC	377
	R^1=SO, R^2=Me, $R^3=CMe_3$, X=O^iPr	MW, DSC	377