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Invited Review

Homogeneous Group 4 metallocene Ziegler–Natta catalysts: the influence of cyclopentadienyl-ring substituents

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Abstract

A new range of metallocene catalysts, Cp_2MCl_2 (M = Ti, Zr, Hf) has been developed in the past decade, which, in the presence of alumoxanes are highly efficient at polymerizing α-olefins (ethene, propene, *etc.*). Variation of the substituents attached to the cyclopentadienyl rings leads to changes in catalyst selectivity and activity.

Further, for α-olefin polymerisation, variations of the ring substituents leads to variation of the tacticity of the polymer product. Studies in which the influence of the ring substituents have been explored have been reviewed.

Key words: Group 4; Cyclopentadienyl; Ziegler–Natta catalyst

1. Homogeneous Ziegler–Natta catalysts

A Ziegler–Natta catalyst may broadly be defined as a material which consists of a Group 3–8 transition metal together with a Group 1, 2 or 13 organometallic, the combination of which is capable of polymerizing olefins and dienes under relatively mild conditions of temperature and pressure [1,2]. In a recent survey of catalyst technology commercialised in the USA during the 1980's [3], polymerisation catalysis was listed as one of four major areas in which innovation has been successfully commercialised [4–6]. Although the catalysts used in industry are mainly heterogeneous, well-defined *homogeneous* Ziegler–Natta catalysts have been developed in the four decades since the original discovery of these types of catalysts. Indeed recently homogeneous catalysts, based on Cp_2MX_2, have provided the impetus for a new generation of polymerisation catalysts. Some examples of these catalysts are shown in Fig. 1.

Herein we review developments that have been made using these homogeneous systems with particular emphasis on the role of the cyclopentadienyl ring in the polymerisation reaction. This review is not intended to provide an exhaustive summary of the literature published in this field, but to highlight results related to the role of ring substituent effects associated with $(CpR)_2MCl_2$ and related systems ($CpR = \eta^5\text{-}C_5H_4R$; M = Ti, Zr, Hf) (Fig. 2). Particular emphasis will be placed on the measurement and interpretation of steric and electronic effects associated with the ring substituents. The polymerisation and co-polymerisation capabilities of these catalysts will be discussed from this perspective. Other applications of these catalysts including mechanistic implications of substituent effects will also be covered briefly. Finally, a summary of work in the fields of cationic Group 4 metallocene and neutral lanthanide metallocene catalysts, again with reference to substituent effects, will be presented. The review covers literature reports up until late 1993.

The new homogeneous Ziegler–Natta catalyst system can polymerise α-olefins (*e.g.* propene, 1-hexene) to isotactic and atactic polymers. Copolymerisation of ethene with α-olefins lowers the polymer density to between 0.90 and 0.98 g cm^{-3}, thus producing LLDPE (Linear Low Density Polyethene) [7]. Terpolymerisation of ethene, propene and a diene has been reported to form EPDM (Ethene Propylene Diene Monomer) elastomers with enhanced light and solvent resistance [7]. It is also possible to polymerise ethene in the presence of starch, cellulose, lignin or $CaSO_4$. The

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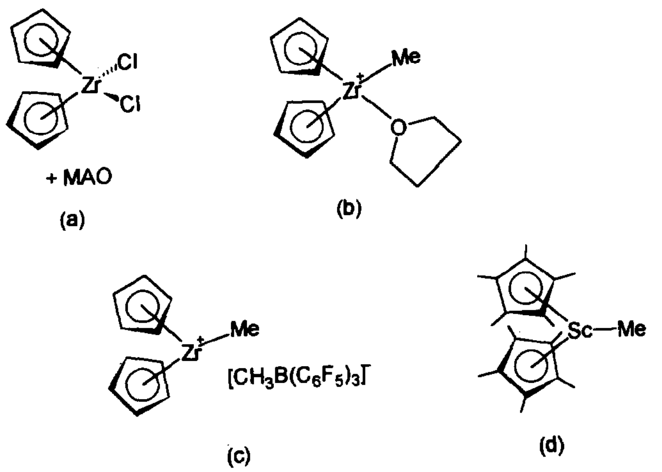


Fig. 1. Examples of homogeneous Ziegler–Natta catalysts: (a) Cp_2ZrCl_2/MAO; (b) $Cp_2Zr(Me)(thf)^+$; (c) $[Cp_2ZrMe][MeB(C_6F_5)_3]$; (d) Cp^*_2ScMe.

resultant polymer combines the physical and chemical properties of natural and synthetic polymers and reduces the inhomogeneities that occur when these components are mixed *after* polymerisation [8–11]. These catalysts can also be mixed with PE (Polyethene) in a solvent and, following solvent removal and admission of ethene, can be used in gas-phase polymerisation reactions [12].

New uses for metallocene catalysts are currently being developed. These include the polymerisation of styrene and methyl methacrylate, copolymerisation of olefins and styrene or cyclodienes, the stereospecific catalysis of Diels–Alder reactions and the chiral synthesis of substituted pyridine derivatives [13]. Novel elastomers and co- and terpolymers produced by these catalysts are expected to have profound commercial impact.

However, there have been major hindrances to the commercialisation of metallocene catalysts, the most important of which has been the need for large amounts of the expensive co-catalyst, MAO (methyl alumoxane). Thus, *supported* metallocene catalysts have been prepared, which also allow for gas-phase polymerisation.

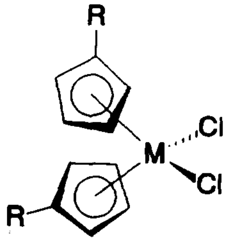


Fig. 2. Monosubstituted $(CpR)_2MCl_2$ ($CpR = \eta\text{-}C_5H_4R$; M = Ti, Zr, Hf) complexes.

Constrained-geometry metallocenes have also been prepared recently for industrial use. Both the above catalysts operate with reduced amounts of alumoxanes, or even without these cocatalysts [13]. Some metallocene-catalysed PE production processes have already been commercialised. Production is mainly for the wire, cable and medical supply market [14] as well as for the film packaging industry [15]. The enhanced properties of these polymers such as clarity, softness, toughness and reduced odour and extractables are brought about by the improved control of MW and short-chain branching which is possible with the new metallocene catalysts. It is thus clear that an understanding of factors which influence the activity of these new metallocene polymers is crucial for optimizing the catalyst. One of these factors relates to the role of the steric and electronic properties of the cyclopentadienyl ring. Prior to a discussion of current information available on these properties, a discussion of the mechanistic information available on the metallocene catalyst will be given.

2. Mechanistic aspects of olefin polymerisation with Group 4 metallocene catalysts

The purpose of this section is not to provide an exhaustive survey of the enormous amount of mechanistic and kinetic investigations which have been carried out on Group 4 metallocene catalysts, but to highlight some important features which have relevance to this review.

2.1. The $(CpR)_2TiCl_2/Et_nAlCl_{3-n}$ ($n = 1$–3) catalyst system

Breslow and Newburg [16], and Natta [17], independently discovered the first homogeneous Ziegler–Natta catalyst, Cp_2TiCl_2/R_2AlCl [18,19]. Much work has subsequently been done to elucidate the mechanism [20–31] and measure the kinetics [32–36] of this and related systems. This work has been thoroughly reviewed by Sinn and Kaminsky [1].

An important feature of these catalyst systems is that tetravalent Ti centres are required for catalytic activity [37]. Small amounts of impurities, such as oxygen and water, increase polymerisation activity as long as the concentration of these impurities is less than that of Cp_2TiCl_2 [1,35,38–41]. Use of MAO as cocatalyst also increases the polymerisation activity [1,42–46]. Spectroscopic investigations have revealed that the active centre is a cationic species, formed in the equilibrium

$$Cp_2TiCl_2 + RAlCl_2 \rightleftharpoons [Cp_2TiR]^+[AlCl_4]^- \quad [26,36]$$

This finding has been supported by numerous chemical and spectroscopic studies [47–49] and it has been confirmed that this cationic centre is responsible for ethene polymerisation [50,51]. It appears that the effects of substituents on the cyclopentadienyl ring on the kinetics of olefin polymerisation have not been investigated.

It is pertinent to this work to briefly highlight the basic mechanism of the $Cp_2TiCl_2/Et_3Al_2Cl_3$ catalyst system. Formation of the active species occurs as depicted in Fig. 3 [52,53]. The role of the aluminium cocatalyst is to alkylate the Ti species and then to activate the resulting Cp_2TiRCl complex by Lewis acid complexation to Cl, or by complete chloride removal. Recently, evidence in favour of the formation of an alkyltitanocenium ion, Cp_2TiR^+, has been published [54]. Polymerisation occurs by olefin coordination to Ti followed by insertion into the Ti–R bond. The catalyst deactivates when Ti^{IV} is reduced to Ti^{III} by bimolecular reductive disproportionation [43] leading to the elimination of polymer chains with saturated and vinyl end-groups.

A recent NMR (^2H, ^{13}C, ^{27}Al) investigation of the interaction between Cp_2TiCl_2 and $MeAlCl_2$ has confirmed many of the basic proposals listed above. However, the study has also implicated the presence of contact and solvent separated ion-pairs on mixing the two species and that the concentration of the solvent separated ion-pair species correlated with ethene polymerisation activity. In arene solvents a third but less active, solvated ion-pair was also detected [55].

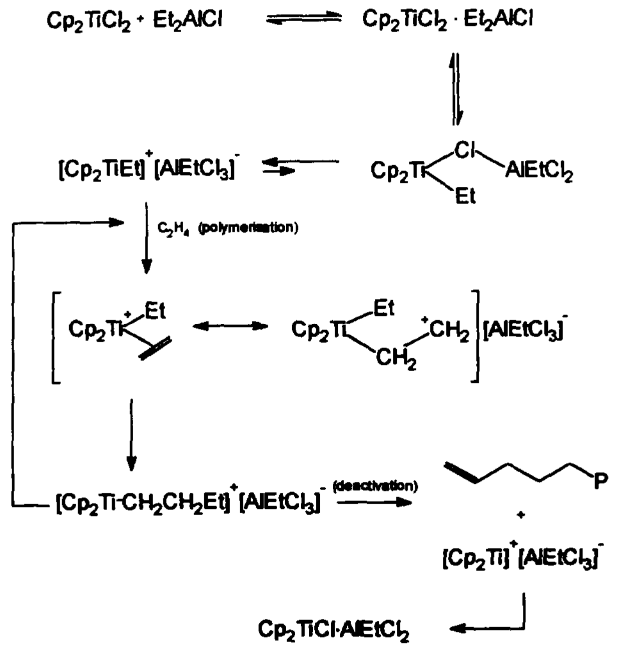


Fig. 3. Mechanism of olefin polymerisation with Cp_2TiCl_2/Et_2AlCl (P = polymer chain.)

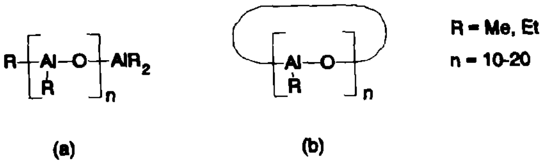


Fig. 4. Generalised structure of aluminoxanes: (a) linear and (b) branched structure.

2.2. The $(CpR)_2ZrCl_2$/alumoxane catalyst system

In polymerisation studies with alumoxane cocatalysts, the focus has been almost exclusively on MAO since it is the most efficient cocatalyst for zirconocene catalysts. The reactions between organoaluminium compounds and water have been studied since the 1960's when alumoxanes were found to be active catalysts for the polymerisation of propylene oxide, monosubstituted epoxides, acetaldehyde, butadiene, *etc.* [56,57]. The generalised structure of alumoxanes is shown in Fig. 4, but it is not known whether alumoxanes comprise a single substance or whether they have a dynamic structure [58,59]. All that is known is that they consist of oligomeric [Al(Me)O] units, in a linear and/or cyclic form [60,61]. Due to their high reactivity towards oxygen and moisture and their incomplete solubility in hydrocarbon and aromatic solvents [62], *characterisation of alumoxanes* is very difficult. This accounts, in part, for the incomplete understanding of their structure and function. Recently, the first structurally characterised alumoxane, $[^tBuAlO]_x$, was reported. Spectral analysis of this compound revealed that the complex is not a linear or cyclic oligomer, but is a cage-compound analogous to the well-known iminoalanes, [RAlNR'] [63].

The *role of alumoxanes as cocatalysts* is not clearly understood, and many functions have been attributed to these compounds. They have been proposed as being responsible for the alkylation of the catalyst [64,65], stabilisation of the cationic metallocene alkyl by acting as a counter-ion [64] and the prevention of bimolecular reduction of the catalyst [45,53,64]. This would account for the large amount of MAO required for good polymerisation activity and chain transfer capabilities [65]. Alumoxanes also scavenge impurities such as water and oxygen from the reaction medium [64]. It has also been proposed that the most important function of alumoxanes is in the formation of the active species. This zirconocene cation is thus stabilised by a so-called "crown-alumoxane" complex.

Although the main polymerisation steps (coordination, insertion, *etc.*) for the metallocene catalyst system

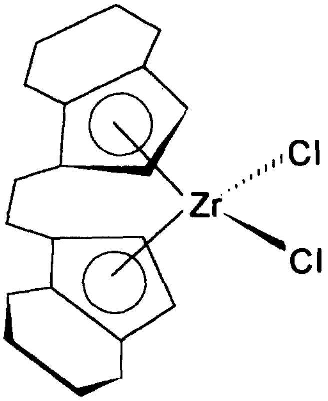


Fig. 5. Structure of $C_2H_4(tH\text{-}Ind)_2ZrCl_2$.

are well understood, the *mechanism*, especially the function of the MAO cocatalyst, is still very much in dispute.

It has been established that the *active centre is a zirconocene cation*, an intermediate which has been postulated for the last three decades [66]. Evidence for this comes from the formation, isolation and ethene polymerisation ability of Cp_2ZrMe^+ complexes (see section 8) and also from other, indirect, investigations. XPS studies on Cp_2ZrMe_2 [67] have shown that the first active species is Cp_2ZrMe^+, which, during polymerisation, becomes Cp_2ZrH^+ [67], or rather $Cp_2Zr(CH_2CH_2R)^+$ [68], which is again active for polymerisation. Also, the reaction of Cp_2ZrCl_2 with $AlCl_3$ leads to the formation of $[Cp_2ZrCl][AlCl_4]$; X-ray crystal structural analysis of this compound showed that the $AlCl_4^-$ moiety is held very loosely at the Zr centre [69]. Recent mechanistic studies using $C_2H_4(tH\text{-}Ind)_2ZrCl_2$ (Fig. 5) have also provided information on the formation of active cationic species [70].

IR spectroscopy has been used to investigate the interaction between MAO and Cp_2ZrCl_2 [71]. It was observed that ν(Al–O) and ν(Al–C) changed when the two components were added. ^1H NMR spectroscopy has revealed that Cp_2ZrCl_2 is monoalkylated by free Me_3Al in MAO, and the formation of a cationic, or at least polarised, complex was observed [72]. Similar results were obtained from a ^{13}C CP-MAS study of $Cp_2ZrMe_2/MgH_2/(Et_2AlCl)_2$ [73]. It is now generally accepted that the first step in the mechanism is alkylation of Cp_2ZrCl_2 by MAO (or free Me_3Al contained therein) and that the resulting $Cp_2ZrMeCl$ then reacts further with MAO to form the active site [74].

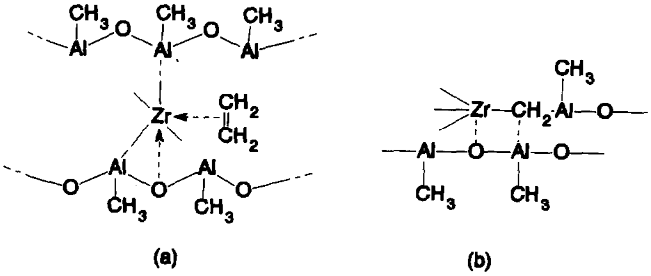


Fig. 6. Possible representations of the Cp_2ZrCl_2/MAO active site.

Although not much is known about the structure of the active site, it is proposed that the Zr moiety is sandwiched between MAO chains as shown in Fig. 6(a) [75]. Other variations on this proposal have been made, *e.g.* that MAO acts as a Lewis base and coordinates to Zr through its oxygen atoms (Fig. 6(b)) [76,77]. The "sandwich" view of the active site is supported by the large excess of alumoxane required for catalytic activity. The polymerisation rate is proportional to $[Zr][Al]^4$ and at low MAO concentrations the activity falls off rapidly because there is no longer enough MAO available to separate the Zr centres [45,65,75–78]. It has also been shown, by ^{14}CO radiolabeling, that at Al/Zr ratios in excess of 1000, all the Zr molecules present form active centres [77,79].

An understanding of *chain transfer processes* is important for polymer MW control. Chain length is determined by the relative rates of propagation (insertion) and chain termination (by chain transfer) [80,81]. Two major means of chain transfer operate for these catalysts:

(1) A dominant *β-H elimination process* [81], which is the main determinant of chain length (Fig. 7).
(2) A *chain transfer to aluminium* [53] (of complexed MAO) (Fig. 7).

As the Zr concentration in the reaction increases, so polymer MW decreases, which can be indicative of a bimolecular reduction deactivation mechanism [43].

Very few investigations of *cyclopentadienyl ring substituent effects on the polymerisation mechanism and kinetics* have been reported. Substituent effects on chain transfer and stereoregularity for Me_2Si-bridged Zr complexes have been studied [82]. Increasing the electron density at the metal increases the polymerisation rate and the rate of chain transfer [83]. This is illustrated by the methyl exchange reactions between Cp_2ZrMe_2 derivatives and different cocatalysts [58]

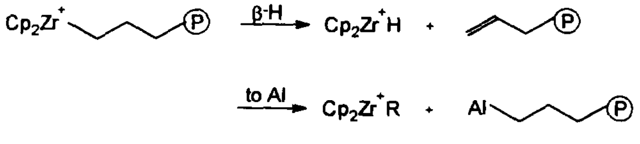


Fig. 7. Chain transfer by β-H elimination and by transfer to aluminium (P = polymer chain).

which have shown that methyl donor strengths decrease in the order μ-$Me_2Si(Cp)_2ZrMe_2 > Ind_2ZrMe_2 > Cp_2ZrMe_2 > Cp_2^*ZrMe_2$, which reflects the relative amounts of metallocene cations formed in each system. It is clear that there is still much to be learnt about alumoxanes and their use as polymerisation cocatalysts.

3. Substituent effects associated with substituted Group 4 metallocene dichlorides

Ligand effects with respect to Ziegler–Natta catalysts have been discussed *qualitatively* as far back as 1971 when Henrici-Olivé and Olivé [84] pointed out that "catalyst tailoring" by modification of the catalyst ligand system could lead to specific changes in catalytic activity and product properties. This requires an understanding of the physical parameters involved in ligand modification. The following factors were judged as the most important in terms of affecting catalyst performance:

(a) The transition metal–olefin interaction: The olefin has a basic character with respect to the metal (M) and therefore acts as an electron-donor. The σ- and π-bonds between the metal and the olefin destabilise the olefin and activate it for insertion. Olefin coordination also destabilises the M–R bond. The stability of olefin coordination to M decreases with increasing olefin size, due to (i) steric factors and (ii) the energies of the olefin orbitals involved in bonding to the metal.

(b) Metal–alkyl bond stability: In a simplified representation of the active centre of a titanocene–aluminium alkyl catalyst system (Fig. 8), fine adjustment of an M–R bond strength is possible by variation of ligand electronic effects. The M–R bond should be unstable, to permit facile opening and olefin insertion to form a new metal–alkyl bond. The stronger the donor properties of Al and the ligands R^1 and R^2, the greater the destabilisation of the M–R bond. The strength of this bond also depends on R itself; stability decreases in the order $Me > Et > (CH_2)_nCH_3$.

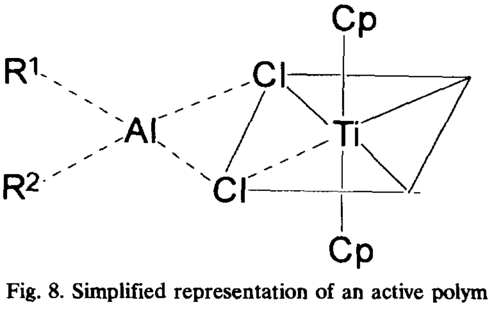


Fig. 8. Simplified representation of an active polymerisation site.

(c) Influence of other ligands, *e.g.* the cyclopentadienyl rings, and substituents attached to the rings: This influence occurs through both the σ- and π-electron systems. If the ligand is a better electron donor, it will reduce the positive charge on the metal and thus weaken the bonding between the metal and all other ligands, particularly the unstable M–R bond which will become more reactive. The action of the π-electron system is superimposed on that of the σ-electron system; a π-acceptor ligand can withdraw electron-density from the π-bonds to other ligands.

(d) Steric effects: Bulky ligands will aid stereospecific olefin coordination and polymerisation. Steric effects affect the coordination of bulky monomers.

The basicity, steric requirements and chiralities of the ligands attached to the metal centre in metallocenes have a strong influence on polymerisation behaviour. The catalyst and reaction intermediates have controlled and well-defined ligand environments, when compared to heterogeneous catalysts [46].

Much work has been performed to investigate the effect of *steric hindrance* at the metal centre on catalyst activity and stereoregulating ability and the effect of variation in *electron density* at the metal centre on activity, molecular weight (MW) and molecular weight distribution (MWD) [46]. This work is discussed below.

4. Quantification of steric and electronic effects associated with substituted cyclopentadienyl ring compounds

Various physical and chemical reactivity probes, as well as theoretical (or computational) methods, have been used in attempts to quantify substituent effects for substituted cyclopentadienyl metal complexes. It is known that the chemical and physical properties of Group 4 bent metallocenes can be varied over a wide range by modification of the substituents on the cyclopentadienyl ring. Even one substituent is sufficient to introduce novel features into the catalytic behaviour, reactivity and stability of these complexes [85,86]. It must be emphasised that the bent metallocenes comprise only one part of the complex Ziegler–Natta catalyst system.

4.1. Physical probes

All the physical techniques reported to date essentially measure the *electronic effects* arising from varying cyclopentadienyl ring substitution.

The measurement of *oxidation potentials* of a series of $(CpMe_n)_2TiCl_2$ complexes ($n = 0$, 3–5) [29] showed that successive methyl substitutions decreased the oxidation potential due to the influence of the substituents on the energies of the valence and inner shell electrons via hyperconjugative effects. The difference in oxidation potential between the un- and pentasubstituted complexes was approximately 0.5 V. No steric effect was noted. The *reduction potentials* of a series of $(CpR)_2ZrCl_2$ complexes ($R = H$, Me, Et, $SiMe_3$) were shown to correlate with increasing electron-donating influence [87]. The half wave potentials ($E^{red}_{1/2}$) increased in the order $SiMe_3 < H < Me < Et$, which showed that the trimethylsilyl group has a poor inductive influence on the cyclopentadienyl ring. This result is also substantiated by the work of Okuda [88], who showed that the ease of reduction of a series of $(Cp\{SiMe_3\}_n)_2ZrCl_2$ complexes ($n = 0$–2) decreases in the order $n = 2 > 1 > 0$. From these data it was concluded that the $SiMe_3$ group is electron withdrawing. This conflicts with other results (see below). Multiple Me_3Si-substitution in a series of $(Cp\{SiMe_3\}_n)_2MCl_2$ complexes ($M = Ti$, $n = 2$; $M = Zr$, $n = 0$–2; $M = Hf$, $n = 2$) has also been investigated by *cyclic voltammetry*. The half-wave potential decreased with increasing substitution, as expected [89].

The *transition metal inner-shell electron binding energies* (BE) of metallocenes have also been used as a measure of substituent effects. As the electron-donating ability of the substituents increases, so the BE decreases. ESCA (*Electronic Spectroscopy for Chemical Analysis*) studies on a series of $Cp'Cp''_2MCl_2$ complexes ($Cp'Cp'' = Cp_2$, $CpCp^*$, Cp^*_2, $M = Ti$, Zr, Hf) showed that the transition from Cp_2MCl_2 to $Cp^*_2MCl_2$ reflected a 1-electron reduction of the complexed metal, and that the BE was not structure-dependent but directly related to the degree of methyl substitution within a series of compounds [90]. XPS studies on a series of $(CpMe_n)(CpMe_m)HfCl_2$ compounds ($n, m = 1$, 3, 5) revealed a linear correlation between increasing degree of methyl substitution and the corresponding decrease in BE [91]. Crystal structural analysis of the compounds confirmed that the BE decrease is due to direct through-bond electron donation and not as a result of structural changes. The methyl groups bend out of the cyclopentadienyl ring plane to relieve steric strain, but this does not alter their ability to donate electron density to the ring and thus to the metal. A similar study involving $(Cp\{SiMe_3\}_n)_2MCl_2$ complexes ($M = Zr$, $n = 0$–3; $M = Hf$, $n = 0$, 3) showed that the trimethylsilyl group is approximately 1.25 times more electron-donating than the methyl group in this class of compounds [92].

Gas-phase ETE (*Electron Transfer Equilibrium*) studies have been used to establish the *ionisation energies* for a series of alkylated nickelocenes, (RCp)(R'Cp)Ni (R, R' = H, Me, Et, ${}^tBu$) [93]. The ionisation energies decreased with the increasing number and size of substituents. The *free energies of electron attachment* for the same complexes became more endoergic with methyl-substitution, but more exoergic as the size of the groups increased. The values obtained did not correlate with the Taft [94] σ_I electronic parameters. The authors concluded that substituent effects could not be described merely in terms of uniform electron donation in redox processes, but that more detailed models were required. Free ionisation energies have also been determined for Cp'Cp''Ru complexes, including $Cp'Cp'' = Cp_2$, $CpCp^*$, Cp^*_2, $(CpSiMe_3)_2$ and $(CpSiMe_3)Cp^*$ [95]. On a relative scale of 0.0 for Cp_2 and -1.0 for Cp^*_2, the electron-donating ability of the $SiMe_3$-group was estimated to be -0.7. The ionisation energies did not correlate well with the corresponding half-wave potentials, but there was an overall trend. As above, there was a poor correlation with the Taft [94] electronic parameters.

Ultra-violet photoelectron spectroscopy (UPS) has been used to investigate the effect of methyl substitution on a series of $(CpMe_n)_2Ti^{III}Cl$ complexes ($n = 1$, 3–5). The effect of increasing methyl substitution on the decrease in ionisation energies is additive within a series. There are no spectral features which might suggest any significant changes in orbital mixing and the prevailing effect is thus electronic and not due to steric congestion [96].

NMR spectroscopy also provides a measure of substituent effects and has been used to study electronic effects in several compound classes, notably those with Group 15 donor ligands [97]. Several workers [98,99] have found that increasing methyl substitution in the series of compounds $(CpMe_n)(CpMe_m)TiCl_2$ ($n = m = 0$, 1, 3, 5; $n = 0$, $m = 1$, 3, 5) caused a downfield shift in the ${}^{49}Ti$ resonance (approximately 150 ppm per Cp^* group). Me_3Si-substitution also caused a downfield shift, indicating that the group is electron-donating. Electron-withdrawing substituents such as Cl^- and CF_3^- also produced a downfield shift, and it was thus concluded that the ${}^{49}Ti$ resonance is not a very good measure of electron density at the Ti centre for these complexes. Recently, Ti NMR data published by Okuda [100] for a series of (multiply) substituted CpR_nTiCl_3 compounds ($R = Me$, $SiMe_3$, ${}^tBu$) have shown that downfield shifts of the Ti resonances occur upon the introduction of electron-donating groups. On this basis, the Me- and ${}^tBu$-groups were found to be more electron-donating than the Me_3Si-group. ${}^{103}Rh$ NMR spectroscopy [101] has also been used to determine the substituent effects for a series of $(CpR)Rh(CO)_2$ complexes. The effect of electron-donating and withdrawing substituents is qualitatively consistent with the traditional model of electron back-donation.

IR spectroscopy [101] has also enabled the correlation of ν_{C-O} data with substitution in $(CpR)Rh(CO)_2$

compounds to be assessed. The absolute integrated intensities of the ν_{C-O} stretching band for a series of (CpR)Fe(CO)(L)I complexes have been determined [102]. For fixed L, the intensity decreases with increasing electron-withdrawing ability of R. No steric effect was noted. The combined ν_{C-O} intensities for two carbonyl bands in a series of substituted-cyclopentadienyl tricarbonyl manganese and rhodium complexes also decreased as the electron-withdrawing character of the substituent on the ring increased [103].

Several other techniques of less importance have been used to investigate substituent effects. HPLC analysis [104] of 56 mono- and bis-substituted cyclopentadienyl titanium derivatives indicated that the order of polarity of the complexes depends on the number of carbon atoms in the substituents. This reflects the electron-donating ability of the substituent which decreases the polarity between that cyclopentadienyl group and the metal centre. UV/visible spectroscopic analysis of a series of titanium compounds [99] showed that λ_{max} decreased as the electron-donating ability of the substituent increased and vice versa. However, multiple methyl substitution effects did not correlate very well with this measure.

The results for the $SiMe_3$-substituent are rather interesting with some techniques showing the group to be electron-withdrawing rather than electron-donating. This group is used to influence the stereochemistry of organic reactions and organosilicon compounds are added to heterogeneous catalysts either as external or internal donors to increase catalytic activity and stereospecificity [99]. Some workers maintain that the $SiMe_3$- and ^{t}Bu-groups are sterically similar and thus exhibit different electronic effects [99], while others hold that the $SiMe_3$-group is a weaker σ-donor and π-acceptor than an alkyl group and thus exerts mainly a steric influence [88]. It has been pointed out that the electron-donating effects of the Me_3Si-group may vary depending on the system under consideration [105].

4.2. Chemical reactivity probes

The rate or equilibrium constant can also be used to assess the influence of steric and electronic effects on the course of a reaction. For example, the rate of the reaction

$$(CpMe_n)_2TiCl_2 + Et_xAlCl_{3-x}(x = 1\text{–}3) \longrightarrow (CpMe_n)_2Ti(AlCl_{4-x}Et_x)(x = 0\text{–}2)(n = 0,1,3)$$

was monitored by visible spectroscopy. The reaction rate was found to decrease as the degree of methyl substitution increased [29]. Clearly, electronic and steric effects cannot be separated here. Similarly, the rate constants for the reaction $(CpR)CpTiCl_2 + 2Me_3Al \rightarrow (CpR)CpTiCH_2AlMe_2Cl + AlMe_2Cl + CH_4$ increase in the order (for CpR) Cp* < $CpMe_3$ < CpMe < $CpSiMe_3$ < $CpPh_2$ < Cp. The rate decreases with both increasing steric size and electron-donating ability of the substituents. The 1,3-diphenyl substituent was shown to be relatively electron-withdrawing, compared to the alkyl groups [106]. Again, steric and electronic effects cannot be separated in this case. The cleavage rates of a series of titanocene metallacyclobutanes decreased with increasing cyclopentadienyl methyl substitution [99]. Steric effects were found to make only a small contribution to the observed variation in rates.

$Cp^*_2ZrMe^+$ is an oligomerisation catalyst for terminal alkynes, and it might be expected that the lowering of the steric bulk of the Cp* ligand would increase catalytic activity [107]. In fact, the sensitivity of the oligomerisation reaction to the CpR steric bulk is reflected by the selective formation of catalytically inactive compounds if less substituted analogues, such as $(CpR)_2ZrMe^+$ (R = Pr, ^{i}Pr, ^{t}Bu, p-tolyl) are used instead. The deactivation of electrophilic d^0 catalysts by the formation of inactive binuclear compounds is increased when less bulky ligands, which provide less protection to the active species, are used.

Insertion of CH_3CN into $(CpR)_2Zr(Me)(CH_3CN)_2^+$ complexes (R = H, Me) proceeds three times faster for the methyl-substituted analogue. The better methyl donor substituent stabilises the increasing electron density at the metal in the transition state, while the steric effect due to the methyl group is minimal [108].

Alkyne hydroalkylation reactions of, *e.g.* 3-butyn-1-ol with $(CpR)_2TiCl_2/Al_2Me_6$ catalysts (R = H, Me, ^{t}Bu) have also been investigated. No significant variation in yield or regioselectivity was found as R was varied. The authors, for various reasons (see below) proposed that substituent effects would only be seen with multiple substitution on the cyclopentadienyl ring [109].

Substitution on the cyclopentadienyl ring leads to reduced aggregation and enhanced solubility of Zr-derived reagents. For example, the hydrozirconation reagent $(CpMe)_2Zr(H)(Cl)$ is a far better reagent than the commonly used oligomeric $[Cp_2Zr(H)(Cl)]_n$ [86].

4.3. Theoretical approaches

Molecular modelling, molecular orbital approaches and methodologies that use input from both procedures have been applied to metallocene catalysts. In these processes electronic and steric effects are not explicitly differentiated.

The *molecular orbital approach* has mainly been used to investigate stabilization effects in either the ground or excited states [110,111]. In particular the role of α-agostic interactions has been investigated,

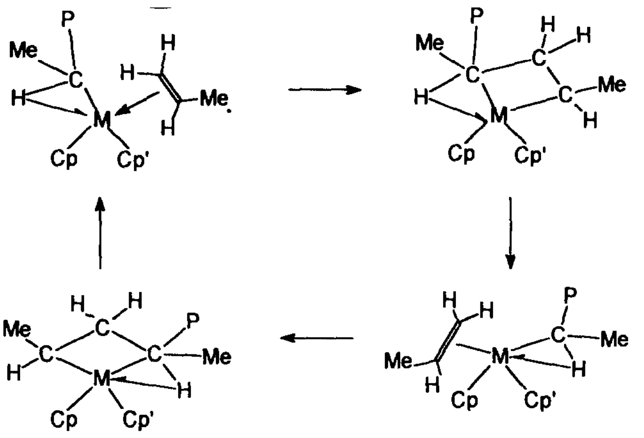


Fig. 9. Polymerisation mechanism involving α-agostic interactions.

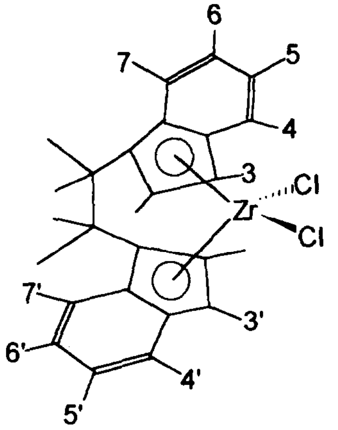


Fig. 10. A substituted $C_2H_4(\eta^5\text{-Ind})_2ZrCl_2$ complex.

since recent studies have implicated their involvement in influencing polymer tacticity [112–114]. Data obtained to date suggest that the agostic interaction can be detected and a mechanism involving this interaction is shown above (Fig. 9) [115].

Molecular Mechanics force fields [116] for linear and bent metallocene [117–120] and half sandwich [121,122] complexes have become available in the past few years. The basic assumption involved in studies employing the molecular mechanics approach to the metallocene catalysts is that non bonded interactions in the transition state will determine the outcome of a polymerisation reaction [113]. The work of Guerra and co-workers has clearly established that molecular structure can be associated with polymer tacticity (propene polymerisation). Recent calculations by Rappé and co-workers [118] using a less rigid model has further indicated the power of a molecular mechanics approach. For a series of $C_2H_4(\eta^5\text{-indenyl})_2ZrCl_2$ complexes in which substitution of the ring system at various positions was investigated (Fig. 10) specific predictions were made:

(a) Substitution at the 4,4′ positions should lead to isotactic polypropene with minimum defects (relative to the unsubstituted complex).
(b) The greater the size of the substituent at the 4,4′ position, the more likelihood there is of syndiotactic defects.
(c) Substitution at other positions *e.g.* 5,5′ *etc.*, will have a marginal effect on enhancing the polymer isotacticity.

The separation of electronic and steric effects by computational procedures as used in other branches of chemistry has also been attempted. To achieve this, measures of steric and electronic properties were required.

An extensive review of *computational methods* used in assessing steric sizes of ligands has recently been published [123]. The Tolman cone angle concept, originally developed to measure the size of trivalent phosphorus donor ligands, has been applied to the cyclopentadienyl ring [124,125]. The size of the cyclopentadienyl ring in metal–Cp and –Cp* complexes has been reported [126].

The *measure of the cone angle for monosubstituted cyclopentadienyl metal complexes* can be approached from two different starting points:

(1) The metal as apex (θ_1): The general procedure used is to calculate the size of a cone which will encompass the ligand with the metal as the apex. A metal–$Cp_{centroid}$ distance of 2.2 Å was chosen to generate the cone, a value consistent with crystal structure data for cyclopentadienylzirconium complexes (see below) (Fig. 11(a)). This method takes into account the degree of substitution of the ring. Since free rotation of the cyclopentadienyl ring about the metal–$Cp_{centroid}$ axis occurs in solution [85,86,109,127–134], the alkyl group R occupies one of the five ring positions only 20% of the time.
(2) The cyclopentadienyl centroid as apex (θ_2): In this method the ring centroid is chosen as apex for a

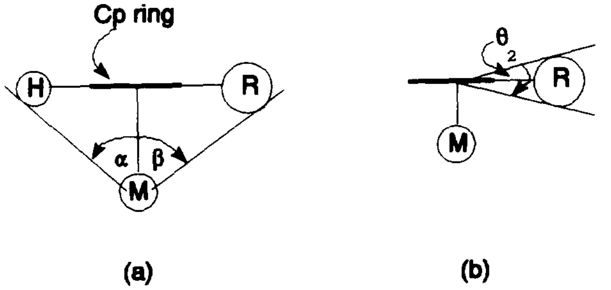


Fig. 11. Measurement of the cyclopentadienyl ring cone angle (a) with metal as apex (θ_1), where $\theta_1 = 2[(4/5)\alpha + (1/5)\beta]$ and (b) with Cp ring centroid as apex (θ_2).

TABLE 1. Ethylene polymerisation reactions of Group 4 metallocene/aluminoxane catalysts

Catalyst [a]	Polymerisation conditions [b]				Activity/ $\times 10^5$ g PE (mol M.h)$^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	T/°C	P/bar			
M = Ti							
$(CpR)_2TiX_2$							
R = H, X = Cl	9.1–20	15.2–43.1	0–50	1.3–8	0.53–344.9	MW	85,172,75
	62.5	12 [d]	50	10	1.9	DSC	145
R = H, X_2 = Cl, Me	9.1	15.2	20	8	191.6	MW	172,75
R = H, X = Me	1.7–9.1	15.2–16.8	20–36	8	19.2–528.8	MW, NMR	172,75,40
R = H, X = Ph	0.29–5.8	4.9–24.2	50	3.0–3.6	86–171	MW	46,59
R = Me, X = Cl	62.5	12 [d]	50	10	0.13	DSC	145
R = Et, X = Cl	62.5	12 [d]	50	10	0.07	DSC	145
R = ^{i}Pr, X = Cl	62.5	12 [d]	50	10	0.05	DSC	145
R = ^{t}Bu, X = Cl	62.5	12 [d]	50	10	0.003	DSC	145
R = $SiMe_3$, X = Cl	62.5	12 [d]	50	10	0.07	DSC	145
R = CMe_2Ph, X = Cl	62.5	12 [d]	50	10	0.002	DSC	145
CpR = $CpMe_4{}^{i}Pr$, X = Cl	20	43.1	0–50	1.3	0.01–0.18	—	85
$(CpR)CpTiCl_2$							
R = Me	62.5	12 [d]	50	10	1.70	DSC	145
R = ^{t}Bu	62.5	12 [d]	50	10	1.12	DSC	145
R = $SiMe_3$	62.5	12 [d]	50	10	0.41	DSC	145
R = CMe_2Ph	62.5	12 [d]	50	10	0.03	DSC	145
CpR = $CpMe_4{}^{i}Pr$	20	43.1	0–50	1.3	0.35–1.7	—	85
M = Zr							
$CpZrCl_3$	0.48–48	5.1–51.4	25–90	1.4–2.5	3.3–295.8	MW	53
$(CpR)_2ZrX_2$							
R = H, X = Cl	0.03–50	2.5–102	0–90	1–8	4.3–36488	MW, NMR, DSC	46,53,65, 71,74,75, 142–144, 171,172, 216,245–248
	6.25	270 [a]	70	10	1.9	DSC	145,249
R = H, X = Me	0.002–0.3	2.2–15.3	20–90	3–8	65.7–22623	MW	45,59,75, 172,250,249
R = H, X = Ph	0.29	5.1	50	3	898	MW	59
R = H, X = CH_2Ph	0.30	4.3	50	3	1054	MW	59
R = H, X = CH_2SiMe_3	0.32	4.5	50	3	1551	MW	59
R = Me, X = Cl	Al/Zr = 24000		80	4.3	1831	MW	46,249
	6.25	270 [e]	70	10	1.7	DSC	145,249
R = Et, X = Cl	3.6	38–61.5	70–80	4.3–7.5	24.7–1200	MW	46,143, 144,249
	4.6–17.7	270–290 [e]	50–80	8–12	2.5–12.6	DSC	145
R = ^{n}Pr, X = Cl	3.6	38–61.5	70	7.5	11.1–179	MW	143,144,249
R = ^{i}Pr, X = Cl	3.2–3.6	38–61.5	70	7.5	34.1–557.8	MW	143,144,249
	6.25	270 [e]	70	10	1.9	DSC	145,249
R = ^{n}Bu, X = Cl	—	—	—	—	—	—	249
R = ^{t}Bu, X = Cl	3.4	38	70	7	299	-	71,144
	6.25	270 [e]	70	10	8.6	DSC	145,249
R = $SiMe_3$, X = Cl	3.2	38	70	7	381–701	MW	71,144
	6.25	270 [e]	70	10	4.9	DSC	145
R = CMe_2Ph, X = Cl	6.25	270 [e]	70	10	1.7	DSC	145
R = NM, X = Cl	0.35–35.5	5.0–64.6	10–90	0.6–2	1.0–456	MW, NMR, DSC	78,142
R = cyclohexyl, X = Cl	—	—	—	—	—	—	249
CpR = $Cp^{i}Pr_2$, X = Cl	3.4–3.6	38–61.5	70	7.5	22.4–362.2	MW	143,144
CpR = $Cp^{t}Bu_2$, X = Cl	—	— [e]	—	—	—	—	249
CpR = $Cp(SiMe_3)_2$, X = Cl	6.25	290 [e]	70	10	2.9	DSC	249
CpR = Cp*, X = Cl	1.0	15	20–80	4.3–7	58–278	MW	46,247
CpR = Cp*, X = Me	0.46	24.2	50	3.6	1595	MW	46
$(CpR)CpZrCl_2$							
CpR = Cp*	1.0	15	70	7	399	MW	247

TABLE 1 (continued)

Catalyst [a]	Polymerisation conditions [b]				Activity/ $\times 10^5$ g PE $(\text{mol M.h})^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	T/°C	P/bar			
$(\text{Ind})_2\text{ZrX}_2$							
X = Cl	0.1–3.0	15.0–24.9	50–60	0.71–5	99.4–3101	MW, DSC	251,252
X = Me	0.26–0.35	5.9	50	3	1985	MW	59
X = CH_2Ph	31	15.5	34	0.28	9.2	MW	150
$(4,7\text{-X}_2\text{Ind})_2\text{Zr(CH}_2\text{Ph)}_2$							
X = H	31	15	34	0.28	11.0	MW	150
X = Me	7.8–31	15–15.5	25–34	0.28–0.75	10.2–138	MW	150,83
X = OMe	31	15	34	0.28	0.6	MW	150
X = F	31	15	34	0.28	4.6	MW	150
$(5,6\text{-X}_2\text{Ind})_2\text{ZrCl}_2$							
X = H	6.9	13.9	25	0.75	140	MW	83
X = Me	5.6	11.2	25	0.75	252	MW	83
X = OMe	4.3	8.7	40	3	12.2	MW	83
X = Cl	3.6	7.2	25	0.75	190	MW	83
$\text{C}_2\text{H}_2(\text{Ind})_2\text{ZrCl}_2$	3.2–31.3	26.6	30–50	0.71–2	92.9–118	MW, NMR DSC	251, 142
$\text{C}_2\text{H}_4(5,6\text{-X}_2\text{Ind})_2\text{ZrCl}_2$							
X = H	6.9	13.9	25	0.75	100	MW	83
X = Me	5.6	11.1	25	0.75	222	MW	83
X = OMe	4.3	8.7	40	3	12	MW	83
$\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2\text{ZrCl}_2$	7.7	15.4	25	0.75	130	MW	83
$\text{C}_2\text{H}_4(\text{tH-Ind})_2\text{ZrCl}_2$	31.3–40	10–26	30–40	1–2	9.5–63	NMR, MW, DSC	142,173
$\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$	1.4–31.3	4–26	30–65	2–5	106–192.9	MW, NMR, DSC	142,253
$\text{Ph}_2\text{Si(Ind)}_2\text{ZrCl}_2$	31.3	26	30	2	58	NMR, MW, DSC	142
$(\text{PhCH}_2)_2\text{Si(Ind)}_2\text{ZrCl}_2$	31.3	26	30	2	35	NMR, MW, DSC	142
$\mu\text{-C}_2\text{H}_4\{\text{Me}_2\text{Si}\}_2(\text{Ind})_2\text{ZrCl}_2$	9.1	4.0	65	5	64.8	MW	253
$\text{Me}_2\text{C(Ind)(Cp)ZrCl}_2$	31.3	26	30	2	4.4	NMR, MW, DSC	142
$\text{Me}_2\text{C(Ind)(CpMe)ZrCl}_2$	31.3	26	30	2	7.7	NMR, MW, DSC	142
$(\text{Flu})_2\text{ZrMe}_2$	0.31	4.7	50	5	< 0.1	MW	253
$\text{Me}_2\text{C(Flu)(Cp)ZrCl}_2$	20–31.3	10–26	30–40	1–2	5.7–6.9	NMR, MW, DSC	142,173
$(\text{CpR})_2\text{HfX}_2$							
R = H, X = Cl	0.09–48	15–56	25–70	1.7–8	4.9–928	MW	172,75,85
R = H, X = Me	0.09–0.3	4.5–15	50–70	3–8	50–856	MW	172,59
R = H, X = Ph	0.30	3.7	50	3	87	MW	59
R = H, X = CH_2SiMe_3	0.30	4.5	50	3	307	MW	59
R = Me, X = Cl	6.25	290 [e]	70	10	2.3	DSC	145
R = Et, X = Cl	6.25	290 [e]	70	10	1.1	DSC	145
R = ^{t}Bu, X = Cl	6.25	290 [e]	70	10	1.3	DSC	145
R = SiMe_3, X = Cl	6.25	290 [e]	70	10	1.6	DSC	145
$\text{C}_2\text{H}_4(\text{Ind})_2\text{HfCl}_2$	31.3	26	30	2	8.3	NMR, MW DSC	142

[a] Cocatalyst is methylalumoxane (MAO) unless specified otherwise; [b] solvent is toluene unless specified otherwise; [c] NMR = ^{13}C NMR spectroscopy, MW = molecular weight, DSC = differential scanning calorimetry; [d] cocatalyst is $\text{Et}_3\text{Al}_2\text{Cl}_3$; [e] Cocatalyst is ethylalumoxane (EAO).

cone which incorporates the ligand groups (Fig. 11(b)). This measure does not distinguish between different degrees of cyclopentadienyl ring substitution.

These cone angle measurements have been used in correlations with experimental data. For example, a linear correlation was found between θ_2 and Δ(H2–H5) (the difference between the *ortho* cyclopentadienyl

TABLE 2. Propylene polymerisation reactions of Group 4 metallocene/aluminoxane catalysts

Catalyst [a]	Polymerisation conditions [b]				Activity /× 10^4 g PP $(\text{mol M.h})^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	T/°C	P/bar			
M = *Ti*							
(CpR)$_2$TiX$_2$							
R = H, X = Me	1.7	16.8	36	–	0.6	NMR, MW	40
R = H, X = Ph	125–400	18–410	−85–50	–	1.2–60.8	NMR, MW, DSC	147,254
R = ^{i}Pr, X = Cl	Al/Ti = 290–500		−50–10	–	3.7–7.0	NMR	255
R = ^{i}Pr, X = Ph	Al/Ti = 230–270		−50–10	–	0.7–2.1	NMR	255
C$_2$H$_2$(Ind)$_2$TiCl$_2$	215	24	−60	–	1.8	NMR, MW	147
C$_2$H$_2$(Ind)(CpMe$_4$)TiX$_2$							
X = Cl	27	54	−20–25	–	12–22 [d]	NMR	256,257
X = Me	27	54	−20–25	–	150–1480 [e]	NMR	256
H(Me)C(Ind)(CpMe$_4$)TiCl$_2$	27	54	50	1.5	37.5	MW, XRD, DSC	258
M = *Zr*							
(CpR)$_2$ZrCl$_2$							
R = H	11–167	16–210	0–60	1–8	23–257	NMR, MW, DSC, IR	60,142, 147,173, 259
R = Me	44	210	50	8	280	MW, IR	60
R = ^{t}Bu	44	210	50	8	200	MW, IR	60
R = NM	31.3	26	30	2	27	NMR, MW, DSC	142
R = CH(Me)(Ph)	Al/Zr = 830–3400		−79– −50	—	1.2–1.3	NMR	260
R = CH(Me)(cyclohexyl)	104	96	−50	—	1.4–2.6	NMR, MW	134,156
R = CH(Me)(Ph)	200	107	−50	1	0.3	NMR, MW	134,156
R = CH(CH$_2$R)(cyclohexyl)	Al/Zr = 970		−50	—	1.2	NMR	134
R = CH(CH$_2$R)(Ph)	Al/Zr = 1000		−50	—	0.5	NMR	134
R = CH(^{i}Pr)(9-BBN)	64–124	83–158	−50	1	0.5–1.4	NMR, MW	155
R = CH(CHMePh)(9-BBN)	48–96	90–96	−50	1	0.3–1.2	NMR, MW	155
R = CH(cyclohexyl) (CH$_2${9-BBN})	84	83	−50	1	1.2	NMR, MW	154,156
R = CH(Ph)(CH$_2${9-BBN})	80	81	−50	1	0.5	NMR, MW	154,156
CpR = Cp{1,2-Me$_2$}	44	219	50	8	375	MW, IR	60
CpR = Cp{1,3-Me$_2$}	44	219	50	8	563	MW, IR	60
CpR = Cp{1,2,3-Me$_3$}	4.4–44	50–219	50	4–8	225–750	MW, IR	60
CpR = Cp{1,2,4-Me$_3$}	44	219	50	8	867	MW, IR	60
CpR = Cp{1,2,3,4-Me$_4$}	44	219	50	8	650	MW, IR	60
CpR = Cp*	6.7–44	16–219	20–50	4–8	30–300	MW, IR	60,247
(Cp*)CpZrCl$_2$	10–318	16–91	−30–50	—	0.9–140	MW, NMR	46,247
C$_2$H$_4$(Cp{3-R})$_2$ZrCl$_2$							
R = Me	10.3	20.6	40	3	372	NMR, MW, DSC	158
R = ^{i}Pr	10.3	20.6	40	3	270	NMR, MW, DSC	158
R = ^{t}Bu	10.3	20.6	40	3	48	NMR, MW, DSC	158
{Me$_2$C}$_2$(Cp{2-^{t}Bu)$_2$ZrCl$_2$	62.5	19.4	50	2	18	NMR, MW, DSC	82
Me$_2$Si(Cp{2-R^1,4-R^2})$_2$ZrCl$_2$							
R^1 = ^{t}Bu, R^2 = H	62.5	19.4	50	2	72	NMR, MW, DSC	82
R^1 = ^{t}Bu, R^2 = Me	62.5	19.4	50	2	102	NMR, MW, DSC	82
R^1 = ^{i}Pr, R^2 = Me	62.5	19.4	50	2	608	NMR, MW, DSC	82
Me$_2$Si(CpR$_n$)(CpR′$_n$)ZrCl$_2$							
R$_n$ = 2,3,5-Me$_3$, R′$_n$ = 2,4,5-Me$_3$	4.0	40	30	3	159	NMR, MW, DSC	159,261
R$_n$ = 2,4-Me$_2$, R′$_n$ = 3,5-Me$_2$	4.0	40	30	3	1 110	NMR, MW, DSC	159,261
R$_n$ = 3-^{t}Bu,R′$_n$ = 4-^{t}Bu	4.0	40	30	3	31	NMR, MW, DSC	159,261
R$_n$ = 3-Me,R′$_n$ = 4-Me	4.0	40	30	3	1 630	NMR, MW, DSC	159,261
R$_n$ = 2,4-Me$_2$, R′$_n$ = 3- or 4-Me	4.0	40	30	3	254	NMR, MW, DSC	159,261
R$_n$ = 3,4-Me$_2$,R′$_n$ = 3-Me	4.0	40	30	3	194	NMR, MW, DSC	159,261
R$_n$ = 3-^{t}Bu, R′$_n$ = 3- or 4-Me	4.0	40	30	3	591	NMR, MW, DSC	159,261
R$_n$ = 2,3,5-Me$_3$,R′$_n$ = H	4.0	40	30	3	735	NMR, MW, DSC	159,261

TABLE 2 (continued)

Catalyst [a]	Polymerisation conditions [b]				Activity $/\times 10^4$ g PP $(\mathrm{mol\ M.h})^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	T/°C	P/bar			
$R_n = 2,4\text{-}Me_2, R'_n = H$	4.0	40	30	3	523	NMR, MW, DSC	159,261
$R_n = 3\text{-}{}^tBu, R'_n = H$	4.0	40	30	3	794	NMR, MW, DSC	159,261
$R_n = 3\text{-}Me, R'_n = H$	4.0	40	30	3	669	NMR, MW, DSC	159,261
$\{Me_2Si\}_2(Cp\{3,4\text{-}Me_2\})_2ZrCl_2$	Al/Zr = 1200		—	2	—	NMR	262
$(Ind)_2ZrCl_2$	13	61.1	50	0.71	41.4	NMR, MW, DSC	251
$(Ind\text{-}R)_2ZrCl_2$							
R = 3-α-cholestanyl	68	73	−30	—	1.5	NMR, MW	154,263
R = neoisomenthyl	100	56–70	−30– −5	1	2.2–3.2	NMR, MW	138,154
R = neomenthyl	100	56–91	−30– −5	1	2.7–20.1	NMR, MW	138
$(tH\text{-}Ind)_2ZrCl_2$							
R = neoisomenthyl	100	60–73	−30– −5	1	3.3–34.7	NMR, MW	138
R = neomenthyl	100	57–64	−30– −5	1	5.7–8.2	NMR, MW	138
$C_2H_4(Ind)_2ZrCl_2$	0.7–200	0.12–420	−55–80	0.71–3	0.04–4300	NMR, MW, DSC, XRD,	8,18,74, 142,158,251, 261,264–271
$C_2H_4(3\text{-}MeInd)_2ZrCl_2$	6.4	20	50	—	1 036 [g]	NMR, MW, DSC	272
$C_4H_4(5,6\text{-}X_2Ind)_2ZrCl_2$							
X = H	7.9	15.9	40	3	2 700	NMR, MW, DSC	83
X = Me	6.8	13.5	40	3	3 200	NMR, MW, DSC	83
X = OMe	5.9	11.8	40	3	36	NMR, MW, DSC	83
$C_2H_4(4,7\text{-}Me_2Ind)_2ZrCl_2$	6.1	12.1	40	3	780	NMR, MW, DSC	83
$C_2H_4(tH\text{-}Ind)_2ZrCl_2$	5.2–62.5	3.8–810	−50–80	1–3	0.14–625 [d]	NMR, MW, DSC, IR	8,18,74,82, 142,158,162, 173,247,264, 265,267, 272–274
$Me_2C(Ind)_2ZrCl_2$	—	6	70	—	2 700	NMR, MW	162
$Me_2Si(Ind)_2ZrCl_2$	1.0–31.3	6–26	30–70	2	312–11 200	NMR, MW, DSC	142,161,162, 253,272
$Ph_2Si(Ind)_2ZrCl_2$	31.3	26	30	2	347	NMR, MW, DSC	142
$(PhCH_2)_2Si(Ind)_2ZrCl_2$	31.3	26	30	2	43	NMR, MW, DSC	142
$C_2H_4\{Me_2Si\}_2(Ind)_2ZrCl_2$	1.2	6.7	65	—	0.0 [f]	—	253
$Me_2Si(Ind\{2\text{-}R^1,5\text{-}R^2\})_2ZrCl_2$							
$R^1 = Me, R^2 = H$	2.0	6.6	50	—	4 000 [f]	NMR, MW, DSC	161
$R^1 = Et, R^2 = H$	2.0	6.6	50	—	3 000 [f]	NMR, MW, DSC	161
$R^1 = Me, R^2 = {}^iPr$	2.0	6.6	50	—	10 500 [f]	NMR, MW, DSC	161
$(Me)(Ph)Si(Ind\{2\text{-}Me\})_2ZrCl_2$	2.0	6.6	50	—	3 500 [f]	NMR, MW, DSC	161
$Me_2Si(tH\text{-}Ind)_2ZrCl_2$	2.0	6.6	50	—	3 500 [f]	NMR, MW, DSC	161
$\{Me_2Si\}_2(tH\text{-}Ind)_2ZrCl_2$	Al/Zr = 1200		—	2	—	NMR	262
$Me_2Si(tH\text{-}Ind\{2\text{-}Me\})_2ZrCl_2$	2.0	6.6	50	—	1 000 [f]	NMR, MW, DSC	161
(1-neoisopinocamphyl) $(tH\text{-}Ind)_2ZrCl_2$	Al/Zr = 570		−30	—	0.17	MW	275
$Me_2C(Ind)(Cp)ZrCl_2$	31.3	6.0–6.6	30–70	2	29–680	NMR, MW, DSC	142,162
$Me_2Si(Ind)(Cp)ZrCl_2$	—	6	70	—	630	NMR, MW	162
$Me_2C(Ind)(CpMe)ZrCl_2$	31.3	6.6	30	2	64	NMR, MW, DSC	142
$Me_2C(Cp)(Flu)ZrCl_2$	0.3–550	0.8–86.2	25–70	—	2336–29907	NMR, MW, DSC	66,142,162, 173,271,276
$Me_2C(Cp\{3\text{-}Me\})(Flu)ZrCl_2$	—	6	70	—	480	NMR, MW	162
$(Flu\{1\text{-}Me\})_2ZrCl_2$	9.6	17	40–70	18	62.5	—	277
M = Hf							
Cp_2HfCl_2	Al/Zr = 1240–1430		0–50	—	1.7–456.9 [f]	NMR	157
$Cp^*_2HfCl_2$	Al/Zr = 750–1500		0–50	—	164–1 262 [f]	NMR	157
$Me_2Si(CpR_n)(CpR'_n)HfCl_2$							
$R_n = 2,3,5\text{-}Me_3$, $R'_n = 2,4,5\text{-}Me_3$	4.0	40	30	3	30	NMR, MW, DSC	159,261
$R_n = 2,4\text{-}Me_2$, $R'_n = 3,5\text{-}Me_2$	4.0	40	30	3	14	NMR, MW, DSC	159,261

TABLE 2 (continued)

Catalyst [a]	Polymerisation conditions [b]				Activity $/\times 10^4$ g PP (mol M.h)$^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	T/°C	P/bar			
$R_n = 3\text{-}^t\text{Bu}, R'_n = 4\text{-}^t\text{Bu}$	4.0	40	30	3	3	NMR, MW, DSC	159,261
$R_n = 3\text{-Me}, R'_n = 4\text{-Me}$	4.0	40	30	3	161	NMR, MW, DSC	159,261
$R_n = 3\text{-Me}, R'_n = \text{H}$	4.0	40	30	3	6	NRM, MW, DSC	159,261
$C_2H_4(Ind)_2HfCl_2$	1.25–31.3	5–40	−10–70	2–3	4.4–9280	NMR, MW, DSC	142,162,261, 264,272,278
$C_2H_4(tH\text{-}Ind)_2HfCl_2$	2.4–5.5	4.8–9.7	50–80	–	910–3480	NMR, MW, DSC	264,272
$Me_2Si(Ind)_2HfCl_2$	2.0	6.6	50	–	200	NMR, MW, DSC	161
$Me_2C(Cp)(Flu)HfCl_2$	4.8–16.0	15.4	50–70	–	281–1655 [f]	NMR, MW	276,279

[a] Cocatalyst is methylalumoxane (MAO) unless specified otherwise; [b] solvent is toluene unless specified otherwise (all concentrations are expressed per volume of toluene); [c] NMR = ^{13}C NMR spectroscopy, MW = molecular weight, DSC = differential scanning calorimetry, XRD = X-ray diffraction analysis, IR = infrared spectroscopy, $[\alpha]_D$ = optical rotation; [d] activity = 10^4 g PP ([Zr][C_3H_6]h)$^{-1}$; [e] k_p/Ms^{-1}; [f] polymerisation carried out in pure propylene; [g] activity = 10^4 g PP (mol M)$^{-1}$.

ring proton resonances) for a series of (CpR)Fe(CO)(L)I complexes [135]. *Solid angle* calculations have also been used to quantify both the size and shape of cyclopentadienyl ring substituents [121,136].

The Hammet Substituent constant provides a *quantitative measure of an electronic effect* [94]. These constants are widely used in the study and interpretation of organic reactions and mechanisms, and have been used successfully in the prediction of equilibrium and rate constants for a variety of reactions. It has been possible to correlate both IR [102] and NMR [133] parameters associated with (CpR)Fe(CO)(L)I complexes with Hammett substituent parameters and cone angle measures to investigate the interaction between steric and electronic factors.

In summary, the cone angle and Hammett substituent constant measures of steric and electronic parameters associated with substituted cyclopentadienyl rings provided a means of quantifying and separating steric and electronic factors:

(1) Both are expected to be *pure measures* of their respective parameters, which permits separation of steric and electronic effects [137].
(2) Both are *quantitative* measures, thus allowing statistical analysis of correlation to be performed.
(3) Both have values for a *wide range of substituents.*
(4) Both are *universal* measures, *i.e.* the values are independent of the metal centre or the type of complex under investigation.

The issue of torsional isomers cannot be neglected when considering the influence of steric (and electronic) parameters. Non-bridged monosubstituted bent metallocene catalysts can exist in three unique conformations (Fig. 12). Crystallographic analyses suggest that small substituents favour conformer (a); bulky substituents conformer (b) [138,139]. The conformers are believed to be close in energy as exemplified by the structural analysis of $(C_5H_4{}^iPr)_2ZrCl_2$ in which all three conformers were detected in the same single crystal [140].

The effect of torsional isomerism on polymer stereochemistry has been analysed for a series of indenyl substituted zirconium catalysts [136]. In the investigation a series of substituted indenyl derivatives were synthesized and their activity in propene polymerisation in the presence of MAO investigated. A correlation between the degree of polymer isotacticity and the torsional isomer detected was observed when the substituent was neo-isomenthyl. However, less conformer rigidity was observed for the neomenthyl substituted catalyst and this resulted in a less stereoselective catalyst.

5. Substituent effects in polymerisation studies with Group 4 metallocene Ziegler–Natta catalysts

This section highlights the *comparative studies* which have been performed on polymerisation reactions using Cp_2MX_2 complexes (M = Ti, Zr, Hf; X = halide, alkyl) as catalysts. This information, together with results of non-comparative studies, is summarised in Tables 1–3, according to polymerisation type.

5.1. Substituent effects in ethene homopolymerisation (Table 1)

Cyclopentadienyl (Cp), *indenyl* (Ind) and *fluorenyl* (Flu) rings have been used in bent metallocene complexes as polymerisation catalysts. In polymerisation studies with R_2ZrMe_2/MAO (R = Cp, Ind, Flu) the order of activity was found to be Ind > Cp > Flu [59]. The indenyl compound is more active than the cyclopentadienyl analogue due to increased electron-donating ability, whereas steric effects predominate for the Flu ligand.

TABLE 3. Ethylene/α-olefin copolymerisation reactions of Group 4 metallocene/aluminoxane catalysts

Catalyst [a]	Polymerisation conditions [b]					Activity /× 10^5 g PE $(\text{mol M.h})^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	[α-olefin] /[C_2H_4] ratio	T/°C	P/bar			
α-olefin = propylene								
M = Ti								
Cp_2TiX_2								
X = Cl	5	25	0.7–4.0	0	0.71	3.6–8.5	NMR, MW	251
X = Me	1.7	16.8	3.0–16.7	36	-	19.9–70.8	NMR, MW	40
X = Ph	2000–7786	40–100	1500	−60–50	1.8	0.03–0.12	NMR, MW	46,280, 281
$C_2H_4(Ind)_2TiCl_2$	400	60	500	−60	-	0.01	NMR	281
M = Zr								
$(CpR)_2ZrX_2$								
R = H, X = Cl	50	10	0.5–4.2	40–50	1	12.2–15.9	NMR, MW, DSC	173,280
R = H, X = Me	1.5–3.3	25–50	1.7–8.0	20–60	8–9	73–254	NMR, MW	172,280
R = Me, X = Cl	—	—	—	50	—	—	NMR	280
CpR = Cp*	776	40	—	50	1.8	1.6	NMR	280,46
$Me_2Si(Cp)_2ZrCl_2$	—	—	—	50	—	—	NMR	280
$(Ind)_2ZrCl_2$	3.0–13	24.9–61.1	0.4–2.3	50	0.7	55–92	NMR, MW DSC	251
$C_2H_4(Ind)_2ZrCl_2$	5–25	1.3–44.5	0.1–9.0	0–50	0.7	6.3–92	NMR, MW DSC	251,282, 283,284
$C_2H_4(tH\text{-}Ind)_2ZrCl_2$	40	10	0.9–4.0	40	1	12.3–18.3	NMR, MW DSC	173
$Me_2C(Cp)(Flu)ZrCl_2$	20	10	0.9–5.6	40	1	1.0–6.9	NMR, MW DSC	173,283
α-olefin = 1-butene								
M = Zr								
$C_2H_4(Ind)_2ZrCl_2$	5–250	21	—	−20–70	5	-	NMR, MW	285
M = Hf								
$C_2H_4(Ind)_2HfCl_2$	5–250	21	—	−20–70	5	—	NMR, MW	285
α-olefin = 1-pentene								
$(CpEt)_2ZrCl_2$	4.55	293	0.70	60	10	5.4	DSC	145
α-olefin = 1-hexene								
M = Zr								
$(CpR)_2ZrX_2$								
R = H, X = Cl	25–50	10–25	0.2–4.6	40–70	1	12.0–32.2	NMR, MW, DSC	173,174
	4.6	293 [d]	0.2–2.1	50–80	8–12	0.1–2.9	DSC	145
R = H, X = Me	0.1–1.0	17	0.3–1.8	60	4	15.8–28.0	NMR, MW, DSC, IR	8,172
R = Me, X = Cl	4.6	293 [d]	0.83	65	10	1.1	DSC	145
R = Et, X = Cl	4.6	293 [d]	0.35–1.38	60–65	10	0.5–8.5	DSC	145
R = ^{i}Pr, X = Cl	4.6	293 [d]	0.83	65	10	1.0	DSC	145
R = ^{t}Bu, X = Cl	4.6	293 [d]	0.21–2.06	50–80	8–12	0.04–9.1	DSC	145
R = $SiMe_3$, X = Cl	4.6	293 [d]	0.83	65	10	3.4	DSC	145
R = CMe_2Ph, X = Cl	4.6	293 [d]	0.83	65	10	0.6	DSC	145
$C_2H_4(Ind)_2ZrCl_2$	8.3–50	25–140	0.5–4.85	-30–70	—	0.03–68.3	MW, DSC	167,174
$C_2H_4(tH\text{-}Ind)_2ZrCl_2$	40	10	0.4–4.6	40	1	15.3–27.9	NMR, MW, DSC	173
$Me_2C(Cp)(Flu)ZrCl_2$	20–80	10	0.4–1.8	40	1	1.0–2.6	NMR, MW, DSC	173
α-olefin = 1-octene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.35–1.10	60	10	0.35–4.3	DSC	145
α-olefin = 1-nonene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.70	60	10	5.4	DSC	145

TABLE 3 (continued)

Catalyst [a]	Polymerisation conditions [b]					Activity $/\times 10^5$ g PE $(\text{mol M.h})^{-1}$	Analyses [c]	Ref.
	[M]/ 10^{-6} M	[Al]/ 10^{-3} M	[α-olefin] /[C_2H_4] ratio	T/°C	P/bar			
α-olefin = 1-decene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.70	60	10	1.7	DSC	145
α-olefin = 1-undecene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.70	60	10	0.04	DSC	145
α-olefin = 1-dodecene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.70	60	10	0.04	DSC	145
α-olefin = 1-tetradecene								
$(CpEt)_2ZrCl_2$	4.6	293 [d]	0.70	60	10	0.78	DSC	145
α-olefin = 2-methylpropene								
M = Zr								
$C_2H_4(Ind)_2ZrCl_2$	0.05–2.0	21	90–1120	30–50	2–4	0.13–1397	MW, NMR	176
α-olefin = 4-methyl-1-pentene								
M = Zr								
Cp_2ZrCl_2	2.0	21	3.5–10.6	30	2	70.5–121	MW, NMR	176
$C_2H_4(Ind)_2ZrCl_2$	2.0	21	3.5–10.6	30	2	121–128	MW, NMR	176

[a] Cocatalyst is methylalumoxane (MAO) unless specified otherwise; [b] solvent is toluene unless specified otherwise (all concentrations are expressed per volume of toluene); [c] NMR = ^{13}C NMR spectroscopy, MW = molecular weight, DSC = differential scanning calorimetry; [d] cocatalyst = ethylalumoxane.

Several studies have been carried out with *monosubstituted cyclopentadienyl ring complexes*. It is generally difficult to compare results obtained by different workers, since reaction conditions are usually different. In a study of $(CpR)_2ZrCl_2$/MAO catalysts (R = H, ^tBu, $SiMe_3$) the order of activities was found to be $SiMe_3$ > H > ^tBu [71]. The workers proposed that since the ^tBu- and $SiMe_3$-substituents were sterically similar, the differences in polymerisation behaviour were due to electronic effects. A similar study [141] also showed the activity of $(CpSiMe_3)_2ZrCl_2$ to be greater than that of $(Cp^tBu)_2ZrCl_2$. No result for Cp_2ZrCl_2 was reported. These findings contradict other results (see below) which show that as the electron-donating ability of the substituent increases, the polymerisation activity should increase. This trend can be seen in results published by Chien [53], where the order of activity for the $(CpR)_2ZrCl_2$/MAO system is CpR = CpMe > CpEt > CpNM > Cp*. Here, electron-donating ability increases, and steric hindrance decreases, polymerisation activity. Another study on the same catalyst system showed a similar activity order of CpR = CpMe > CpEt > Cp > Cp* [46]. In a similar series of experiments with Cp'Cp''$ZrCl_2$/MAO complexes, the order of activities is dominated by steric effects: Cp'Cp'' = $(CpNM)_2$ > Cp_2 > CpCp* > Cp^*_2 [78], whereas another study showed Cp_2ZrCl_2 to be more active than $(CpNM)_2ZrCl_2$ [142]. Ethene polymerisation with a series of $(CpR)_2ZrCl_2$/MAO catalysts showed the following order of activities: R = $SiMe_3$ > ^iPr > Et > H > ^tBu > ^nPr [143,144]. According to the authors, this trend cannot be explained on the grounds of steric or electronic effects alone. The increase in bulk for the ^iPr substituent should reduce catalytic activity through steric hindrance to approach of the monomer to the Zr centre. The authors proposed that the high activity of this catalyst was due to the generation of hydride centres at Zr involving the α-H of the ^iPr substituent. The difference in reactivity between the catalysts with ^tBu- and Me_3Si-substituents was ascribed to electronic effects.

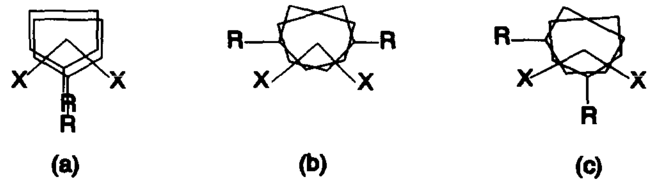


Fig. 12. (a) *syn*-, (b) *anti*- and (c) *gauche*-like conformations for bent metallocene complexes in the solid state.

A comparison of ethylene polymerisation activities of a series of $(CpR)_2MCl_2$ complexes, cocatalysed by ethylalumoxane (EAO), was carried out by the authors [145]. For M = Zr, the order of activities was found to be R = ^tBu > $SiMe_3$ ≈ Et > ^iPr > Me ≈ H ≈ CMe_2Ph. Steric or electronic effects alone could not account for the observed trend in polymerisation activity. However, using a linear combination of cone angles (steric parameter) and Hammett substituent constants (electronic parameter) it was possible to *quantitatively* correlate the polymerisation activities with both steric and electronic parameters associated with the substituents on the cyclopentadienyl rings [146]. The data indicated that an increase in ligand steric size produced a small increase in polymerisation activity while an increase in ligand electron donating ability substantially increased the catalytic activity. The electronic effect was estimated as contributing approximately 80% of the activity change. In the case of M = Hf, the activities for R = Me, Et, ^{t}Bu and $SiMe_3$ were all found to be very similar. Two studies have shown that disubstituted $(CpR_2)_2MCl_2$ complexes (R = ^{i}Pr [141,142], $SiMe_3$ [143]; M = Zr) have lower polymerisation activities than their monosubstituted analogues, presumably due to increased shielding of the Zr centre.

Comparison of these and the preceding results, indicates that a single alkyl substituent increases catalytic activity by the electron-donating enhancement of coordinated anionic propagation. Further, steric bulk, up to a certain point, could stabilise the catalyst, retarding deactivation by bimolecular disproportionation.

Polymer MW's were found to follow the same trend as the polymerisation activities in the $(CpR)_2ZrCl_2$/MAO (CpR = CpH, CpMe, CpEt, Cp*) series [46] (see above). As has previously been shown [147], the reduction in MW is not a necessary consequence of increased termination rates.

Polymer melting points of a series of $(CpR)_2MCl_2$/EAO catalysts (M = Zr: R = H, Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$, CMe_2Ph; M = Hf: R = Me, Et, ^{t}Bu, $SiMe_3$) were found to correlate well with electronic parameters and a contribution from steric factors was found to be statistically not important [144].

Few studies have generated data on the influence of substituent effects using titanocene catalysts. In the first of these an order of activity of Cp_2TiCl_2 > $(CpR)CpTiCl_2$ > $(CpR)_2TiCl_2$ (CpR = $CpMe_4^iPr$) was noted [85]. Cationic titanium complexes have also been used in substituent effect studies. For the system R_2TiMe^+, the order of activities is R = Ind > $CpSiMe_3$ > Cp [148]. Studies on a series of mixed-ring (CpR)$CpTiCl_2$ (R = H, Me, ^{t}Bu, $SiMe_3$, CMe_2Pu) were carried out by the authors [149]. Polymerisation activity was found to be almost totally dependent on steric factors. The existence of a "steric threshold" was demonstrated, with only Cp_2TiCl_2 and the mixed ring titanocenes with sterically less demanding substituents having appreciable polymerisation activity. This limited information is consistent with results found for neutral zirconocene/MAO catalysts [71,59].

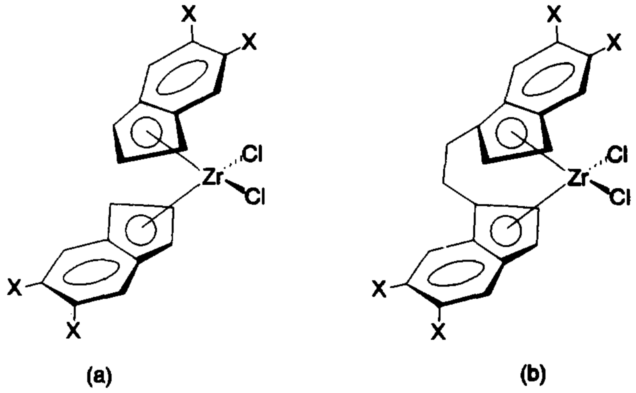


Fig. 13. (a) $(\eta^5\text{-}5,6\text{-}X_2Ind)_2ZrCl_2$ and (b) $C_2H_4(\eta^5\text{-}5,6\text{-}X_2Ind)_2ZrCl_2$ complexes.

Substituted indenyl systems have also been used to investigate substituent effects. Here, the substituents have been attached to the six-membered ring to minimise their steric influence. In the $(\eta^5\text{-}5,6\text{-}X_2Ind)_2ZrCl_2$/MAO system [83] (Fig. 13(a)), the order of ethene polymerisation activities was found to be X = Me > H > 4,7-Me_2 > Cl > OMe and for polymer MW's X = 4,7-Me_2 > Me > H > Cl > OMe. For the $C_2H_4(\eta^5\text{-}5,6\text{-}X_2Ind)_2ZrCl_2$/MAO system [83] (Fig. 13(b)), the order of ethene polymerisation activities was X = Me > 4,7-Me_2 > H > OMe and for MW's X = 4,7-Me_2 > H > Me > OMe. Electron-withdrawing groups, like Cl^-, are expected to decrease catalytic activity and polymer MW. The results indicate that the methoxy substituent may behave as an electron-withdrawing group due to an interaction or reaction with MAO. Electron-donating groups increase catalytic activity, as expected. The 5,6- and 4,7- substituted methyl derivatives should have the same electronic effect and thus the lower activities for the 4,7-substituted derivatives are ascribed to steric hindrance.

The rationalisation of the MW trends is somewhat more complicated and should be considered in the light of the reduced activity which accompanies the MW decreases in these series. There is a drop in the steady-state polymerisation rate and the rate of chain transfer with decreasing electron density at the metal centre. The results for the 4,7-substituted derivatives are influenced by steric effects. The C_2H_4-bridged catalysts have similar polymerisation rates but increased rates of chain transfer due to the increased electron donation from the ethene bridge. This decreases the MW's even further. The decrease in polymerisation rate with decreasing electron density at the metal is suggested to be due to increasing coordination to MAO as the metallocene becomes more electron-deficient. This factor leads to reduction of activity due to the resultant strengthening of the M–C bonds. As the frontier molecular orbitals of the Ind_2Zr moiety

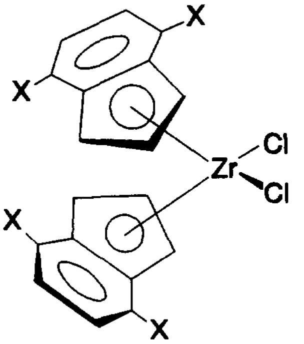


Fig. 14. (η^5-4,7-X_2Ind$)_2$ZrCl$_2$.

decrease in energy, the ground state for olefin insertion becomes stabilised.

A study by Piccolravazzi [150] using (η^5-4,7-X_2Ind$)_2$ZrCl$_2$/MAO catalysts (Fig. 14) gave the order of activities as $X = H \approx Me > OMe > F$ and that of MW's as $X = H > Me > F > OMe$. Here, electron donors have no significant effect on the polymerisation activity. The electronic and steric effects are either too small to be detected (unlikely in the light of the above results [83]) or compensate each other. Electron-withdrawing groups decrease activity and MW, as expected. Again, there are too few data points for the substituted indenyl complexes to really quantify the substituent effects, or even substantiate the claim that 4,7-substituted complexes provide a steric contribution to catalytic behaviour.

A summary of these and other substituted Group 4 metallocene catalysts used for ethene polymerisation studies, together with relevant reaction conditions and analyses, may be found in Table 1.

5.2. Substituent effects in propylene homopolymerisation (Table 2)

In the production of polypropene (PP), both activity and stereospecificity are important, and both must be considered when investigating substituent effects. Unsubstituted, achiral catalysts produce only atactic PP [151]. In 1984, Ewen [145] published the first report on the use of a chiral homogeneous catalyst to produce partially isotactic PP. This was rapidly followed by the development of racemic, bridged indenyl, catalysts by Kaminsky and Brintzinger [152]. These catalysts produced highly isotactic PP with a narrow MWD.

Substituent effects certainly play a large part in determining polymerisation activity in PP production. Cp_2ZrCl_2 has a higher activity and produces a lower polymer MW than Cp*CpZrCl$_2$ in the MAO cocatalysed polymerisation of propene [145]. This is presumably due to steric effects. The influence of both the number and position of methyl substituents on polymerisation activity is shown in a study using (CpR$)_2$ZrCl$_2$ catalysts where the order of activities is CpR = Cp{1,2,4-Me$_3$} > Cp{1,2,3,4-Me$_4$} > Cp{1,3-Me$_2$} > Cp{1,2-Me$_2$} > CpMe > Cp* > Cp{1,2,3-Me$_3$} > Cp^{t}Bu > Cp [60]. The results may be rationalised by a combination of steric and electronic effects. Methyl groups are electron-donating, but steric effects influence cyclopentadienyl ring meshing. The effect would be larger for the 1,3-Me$_2$ derivative than for the 1,2-Me$_2$ or 1,2,3-Me$_3$ compounds as a result of the increase in the $Cp_{centroid}$–M–$Cp_{centroid}$ angle, which would facilitate monomer coordination. (CpNM$)_2$ZrCl$_2$/MAO has a slightly higher polymerisation activity than its unsubstituted analogue. This is ascribed to the slightly higher stereospecificity of the substituted catalyst which, in some cases, leads to higher productivity [140]. This should be compared to the PE results, where the order of activities is reversed.

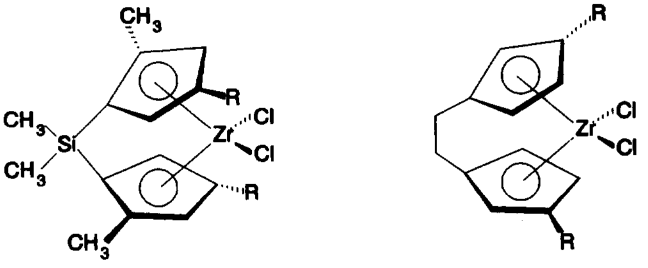
Titanocene activities seem to be dominated by steric effects, as is shown by the decreased activity of (Cp^{t}Bu$)_2$TiPh$_2$/MAO compared to the unsubstituted titanocene [153]. Other substituents were also investigated in this work, but reaction conditions do not permit direct comparison.

The additivity of substituent effects, especially as regards stereoselectivity, is shown in several studies. Isotacticity increases for the (CpCHR^{1}R^2$)_2$ZrCl$_2$/MAO system in the order R^1,R^2 = cyclohexyl (Cy),H < Ph,H < Cy,9-BBN < Ph,9-BBN [154,155]. In a similar polymerisation system, isotacticity increased in the order R^1,R^2 = Me,Cy < Me,Ph < CH$_2$R,Cy < CH$_2$R,Ph [132,156].

Steric effects are further illustrated in propene oligomerisation studies using Cp_2ZrCl_2 and $Cp^*_2ZrCl_2$/MAO [157]. In the case of the unsubstituted compound, β-H elimination is the only chain termination mechanism observed. However, for the pentamethyl derivative, due to steric congestion in the transition state, only β-Me elimination is observed.

Bridged complexes have been used extensively for propene polymerisation since their increased rigidity improves stereoselectivity. Me$_2$Si(Cp{2-Me,4-R}$)_2$ZrCl$_2$/MAO complexes (R = ^{t}Bu, ^{i}Pr) (Fig. 15(a)) have been tested for polymerisation activity (R = ^{t}Bu > ^{i}Pr) and polymer isotacticity (R = ^{i}Pr > ^{t}Bu). The latter trend was suggested to be due to steric factors [82]. Similar results were found for polymerisation studies with *rac*-C_2H_4(Cp{3-R}$)_2$ZrCl$_2$/MAO (R = Me, ^{i}Pr, ^{t}Bu) (Fig. 15(b)). As the steric size of the substituent increased, so activity decreased and isotacticity increased [158].

In a series of Me$_2$Si(CpR$_n$)(CpR'$_n$)MCl$_2$/MAO complexes (M = Zr, Hf; R$_n$,R'$_n$ = Me, ^{t}Bu, 2,4-Me$_2$, 2,3,5-Me$_3$; R$_n$ = 2,3,5-Me$_3$, 2,4-Me$_2$, 3,4-Me$_2$, ^{t}Bu, Me,



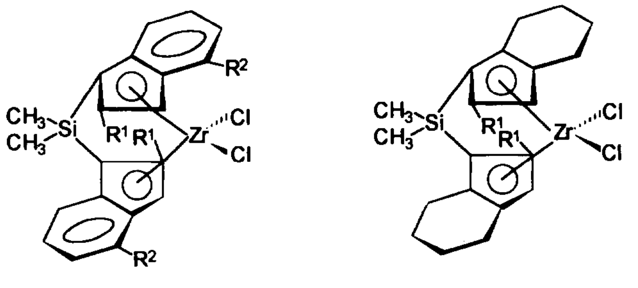
(a) (b)

Fig. 15. (a) $Me_2Si\ (Cp\{2\text{-}Me,4\text{-}R\})_2ZrCl_2$ and (b) *rac*-$C_2H_4(Cp\{3\text{-}R\})_2ZrCl_2$.

R'_n = Me, H), the number, position and type of substituents had a profound influence on polymerisation activity and polymer properties, but no regular trends could be noted from the data [31,159,160].

$C_2H_4(\eta^5\text{-}5,6\text{-}X_2Ind)_2ZrCl_2/MAO$ catalysts (Fig. 13) were also used for propene polymerisation studies. The trend in activities is similar to that found for PE: R = Me > H > 4,7-Me_2 > OMe. The MW's are not as sensitive to changes in the electronic environment of the metal. Catalyst stereospecificity decreased as the electron density at the metal increased [83].

Finally, a breakthrough in polymerisation of propene with zirconocene catalysts in terms of the production of a high MW polymer has been made with the development of substituted-indenyl, Me_2Si-bridged catalysts [161]. In the case of the indenyl derivatives shown in Fig. 16(a), the introduction of a methyl group near the silylene bridge (R^1 = Me, R^2 = H) increased the polymer MW five-fold relative to the unsubstituted derivative. Larger 2-substituents adjacent to the bridge (R^1 = Et) did not result in improved polymer properties. By contrast, a different substituent on the annelated benzene ring (R^2 = ^{i}Pr) yields a further MW increase. This complex is also more active than the unsubstituted catalyst, making it a realistic candidate for technical applications. The effect of changing R^1 can also be seen in the tetrahydroindenyl derivatives (Fig. 16(b)). Replacing H with Me at the R^1 position doubles the polymer MW and increases the isotacticity. From crystal structural analysis of both types of compounds, a direct steric influence of the R^1 group on the chain termination reaction (and thus on MW) is not expected. An electronic effect appears to be dominant. A decrease in the local Lewis acidity at the cationic Zr centre reduces its ability to abstract a β-H atom, thus increasing the polymer MW. Additional alkyl substitution enhances this effect, as does the aromaticity of the 6-membered ring. A less important steric effect is invoked to explain the increased isotacticity of the polymers produced by the substituted catalysts.



(a) (b)

Fig. 16. (a) $Me_2Si(Ind\{2\text{-}R', 4\text{-}R^2\}_2ZrCl_2$ (b) $Me_2Si(tH\text{-}Ind\{2\text{-}R'\})_2ZrCl_2$.

Numerous other "non-comparative" propene polymerisation results using substituted catalysts have been reported in the literature. They are listed in Table 2 for completeness of this summary, together with the results detailed above. A general survey of bridged propylene polymerisation catalysts has been published [162].

5.3. *Substituent effects in styrene and hexene homopolymerisation*

The polymerisation of styrene with titanium based catalysts, in the presence of MAO, has been known for some time [163,164]. The reactions produce syndiotactic polymer. More recently a series of $(\eta^5\text{-}C_5R'_4R)TiX_3$ (R' = Me, Ph, H; R = H, PPh_2, $SiMe_3$; X = O^iPr) and $(Ind)TiX_3$ complexes [165,166] have been prepared and found to catalyse syndiotactic polystyrene formation in the presence of MAO. These half-sandwich complexes gave variable results. The general conclusion drawn by the authors was that small electron donating substituents favoured syndiotactic polystyrene formation at more rapid rates.

Hexene-1 polymerisation has been studied using *rac*-ethene (indenyl) zirconium dichloride /MAO but no systematic studies have been reported [167].

5.4. *Substituent effects in ethene–olefin copolymerisation studies (Table 3)*

5.4.1. *Ethene–propene (EP) and ethene-1-butene (EB) copolymerisations*

EP copolymerisation studies have been carried out with several substituted metallocene systems. Steric effects would appear to be important, although there are too few systematic studies to show this conclusively. The ethene reactivity ratio (r_1) for a series of $(CpR)_2ZrCl_2/MAO$ catalysts (CpR = CpH, CpMe, Cp*) follows the order Cp* > CpMe > CpH. The comparative propene reactivity ratio (r_2) for R = H is larger than that for the pentamethylcyclopentadienyl complex [168], a trend which is purely steric in origin. A similar study showed a trend for r_1 of $Cp^*_2ZrCl_2 > (CpMe)_2ZrCl_2 > (Cp_2ZrCl)_2O > Cp_2ZrCl_2 > Me_2Si(Cp)_2ZrCl_2$; the trend for r_2 was the reverse. Here the ordering was rationalised in terms of steric effects which influence the Cl–Zr–Cl angle and thus facilitate or hinder monomer approach to the metal centre [46].

No other systematic studies have been reported. Other substituted cyclopentadienyl catalysts which have been used for copolymerisation studies are $(CpSiMe_3)_2ZrCl_2$ [169] and $C_2H_4(Ind\{3\text{-}SiMe_3\})_2ZrCl_2$ [170].

5.4.2. *Copolymerisation of ethene with higher α-olefins*

Very little has been reported on this type of copolymerisation. Ethene–1-hexene (EH) copolymers have been produced with Cp_2ZrCl_2/MAO [8,171–173] and a comonomer effect has been observed [174]. The activity of the catalyst changed with the proportion of 1-hexene present in the reaction, viz. the activity increased with hexene concentration up to about 50 mol% and then decreased.

The comonomer effect has also been observed in ethene–1-hexene copolymerisations with the $(CpEt)_2ZrCl_2$/EAO catalyst system. A series of ethene–1-hexene copolymerisations carried out with $(CpR)_2ZrCl_2$/EAO (R = H, Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$, CMe_2 Ph) indicated that the *difference* between homo- and copolymerisation activities for each catalyst could be correlated quantitatively with a combination of steric (cone angle) and electronic (Hammett substituent constant) parameters.

Ethene–1-octene copolymerisations have also been performed with Cp_2ZrCl_2/MAO and $(CpEt)_2ZrCl_2$/EAO [143,175].

5.4.3. *Copolymerisation of ethene with other monomers*

There are very few further reports on copolymerisation studies with substituted metallocenes. Copolymerisations of ethylene with C_5-C_{14} α-olefins using the $(CpEt)_2ZrCl_2$/EAO catalyst system have been carried out [143]. Good activities are obtained up to C_8 after which the polymerisation activity drops considerably, indicating the operation of a steric threshold. Ethene has also been polymerised with 4-methyl-1-pentene and 2-methyl-1-pentene using Cp_2ZrCl_2/MAO and $Et(Ind)_2ZrCl_2$/MAO [176]. The bulkier comonomer is incorporated to a lower extent due to steric hindrance. Ethene and 4-methyl-1-pentene have been copolymerised with $(CpMe)_2ZrCl_2$/MAO/^{i}Bu$_3$Al [177] and $(CpMe)_2Zr(OMe)Cl$/MAO/^{i}Bu$_3$Al [178]. $(CpBu)_2ZrCl_2$/MAO has been used to copolymerise ethene with 1,3-butadiene [179,180] and 1,4-hexadiene [181].

Table 3 summarises the available information on ethene–α-olefin metallocene polymerisation catalysts.

6. Supported substituted Group 4 metallocene catalysts (Table 4)

As mentioned earlier, much work on the development of *supported metallocene catalysts*, particularly as reported in the patent literature, is presently underway. Although these studies fall outside the scope of this review, it is pertinent to mention some examples of substituted metallocene catalysts which have been supported on various materials. The properties of the

TABLE 4. Polymerisation reactions of supported Group 4 metallocene catalysts

Monomer	Comonomer	Catalyst/cocatalyst(s)/support	Analyses [a]	Ref.
Propylene	—	$C_2H_4(Ind)_2ZrCl_2$/MAO/PDA[b]-Me_3Al	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/PDA	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/DA [c]	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/Al_2O_3	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/PDS [d]-Me_3Al	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_1$/MAO/PDS	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/DS [e]	NMR, MW, DSC	267
		$C_2H_4(Ind)_2ZrCl_2$/MAO/SiO_2	NMR, MW, DSC	267
		$C_2H_4(tH\text{-}Ind)_2ZrCl_2$/MAO/PDS-$Me_3Al$	NMR, MW, DSC	267
Ethylene	Propylene	$C_2H_4(Ind)_2ZrCl_2$/MAO/SiO_2	NMR	286
		$C_2H_4(Ind)_2ZrCl_2$/MAO/^{i}BuAO [f]/SiO_2	NMR	286
		$C_2H_4(Ind)_2ZrCl_2$/MAO/^{i}Bu$_3$Al/SiO_2	NMR	286
		$C_2H_4(Ind)_2ZrCl_2$/MAO/Me_3Al/SiO_2	NMR	286
Ethylene	Propylene and ethylidene norbornene	$C_2H_4(Ind)_2ZrCl_2$/MAO/SiO_2	NMR, MW, DSC	287

[a] NMR = ^{13}C NMR spectroscopy, MW = molecular weight, DSC = differential scanning calorimetry, [b] PDA = partially dehydroxylated alumina; [c] DA = dehydroxylated alumina; [d] PDS = partially dehydroxylated silica; [e] DS = dehydroxylated silica; [f] ^{i}BuAO = isobutylaluminoxane.

TABLE 5. Other olefin-related reactions of Group 4 metallocene/aluminoxane catalysts

Reaction type	Catalyst [a]	Analyses [b]	Ref.
Polymerisation of:			
1-Butene	Cp$_2$ZrCl$_2$	NMR, GC–MS	157
	Cp$_2^*$ZrCl$_2$	NMR, GC–MS	157
	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	MW, IR	273
	Cp$_2$HfCl$_2$	NMR, GC–MS	157
	Cp$_2^*$HfCl$_2$	NMR, GC–MS	157
1-Hexene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	—	167
4-Methyl-1-hexene	C$_2$H$_4$(tH-Ind)$_2$Zr (*O*-acetyl-(R)-mandelate)	MW, IR, DSC	288
Cyclobutene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, XRD, DSC	191,193
Cyclopentene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, IR, XRD, DSC	176,191,193
	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	NMR, XRD, DSC	191
	Me$_2$Si(Ind)$_2$ZrCl$_2$	NMR, DSC	193
Norbornene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, XRD, DSC	191,193
Cyclopolymerisation of:			
1,5-Hexadiene	Cp$_2$TiCl$_2$	NMR, $[\alpha]_D$	289
	Cp'ZrCl$_3$, Cp' = Cp, Cp*	NMR	290
	Cp$_2$ZrX$_2$, X = Cl, Me	NMR, MW, $[\alpha]_D$	184,289,290
	Cp$_2^*$ZrCl$_2$	NMR, MW, $[\alpha]_D$	81,184,289,290
	Me$_2$Si(Cp')$_2$ZrCl$_2$, Cp' = Cp, CpMe$_4$	NMR	290
	C$_2$H$_4$(Ind)$_2$Zr(binaphtholate)	NMR, $[\alpha]_D$	289
	C$_2$H$_4$(tH-Ind)$_2$Zr(binaphtholate)	NMR, $[\alpha]_D$	187,289
2-methyl-1,5-hexadiene	Cp$_2^*$ZrMe$_2$	NMR, MW	291
Copolymerisation of ethylene with:			
1,3-Butadiene	Cp$_2$ZrCl$_2$	NMR, MW, IR, DSC	172
Cyclopentene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, MW	192
Cycloheptene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, MW	192
Cyclooctene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, MW	192
Norbornene	Cp$_2$ZrCl$_2$	NMR	191
	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR	191
	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	NMR	193
Dimethanonaphthalene	Cp$_2$ZrCl$_2$	NMR	191
	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR	191
Copolymerisation of propylene with:			
1-Hexene	Cp$_2$ZrCl$_2$	NMR, MW, DSC	173
	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	NRM, MW, DSC	173
	Me$_2$C(Cp)(Flu)$_2$ZrCl$_2$	NMR, MW, DSC	173
Cyclopentene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR	193
Copolymerisation of:			
Cyclopentene and allyltrimethylsilane	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	NMR, IR, $[\alpha]_D$	191
Terpolymerisation of:			
Ethylene, propylene and 1,5-hexadiene	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, MW	190
Ethylene, propylene and ethylidene norbornene	Cp$_2$ZrMe$_2$	NMR, MW	172
	C$_2$H$_4$(Ind)$_2$ZrCl$_2$	NMR, MW, DSC	287
Oligomerisation of:			
Propene	Cp$_2$ZrCl$_2$	NMR, GC	292
	Cp$_2^*$ZrCl$_2$	NMR, GC	292
	C$_2$H$_4$(tH-Ind)$_2$Zr-bis(*O*-acetyl-(R)-mandelate)	GC, NMR, MS, $[\alpha]_D$	201
	Cp$_2^*$HfCl$_2$	NMR, GC	292
1-Butene	C$_2$H$_4$(tH-Ind)$_2$ZrCl$_2$	GC, NMR, MS, $[\alpha]_D$	201,176
1-Hexene	Cp$_2$ZrCl$_2$	GC	206
1-Octene	Cp$_2$ZrCl$_2$	GC	207

TABLE 5 (continued)

Reaction type	Catalyst [a]	Analyses [b]	Ref.
Hydrooligomerisation of:			
Propene	$C_2H_4(tH\text{-}Ind)_2ZrX_2$, X = Cl, Me	DSC, $[\alpha]_D$, NMR, GC, MS, IR	205,293,294
Cyclopentene	Cp_2ZrCl_2	GC, MS, NMR	295
	$C_2H_4(Ind)_2ZrCl_2$	GC, MS, NMR	295
Hydrogenation of:			
1-Pentene	$C_2H_4(tH\text{-}Ind)_2ZrMe_2$	GC	198
1-Decene	$C_2H_4(tH\text{-}Ind)_2ZrMe_2$	GC	198
cis-2-Hexene	$C_2H_4(tH\text{-}Ind)_2ZrMe_2$	GC	198
trans-2-Hexene	$C_2H_4(tH\text{-}Ind)_2ZrMe_2$	GC	198
Styrene	$C_2H_4(tH\text{-}Ind)_2ZrX_2$, X = Me, Cl	GC	198
	$C_2H_4(tH\text{-}Ind)_2Zr$-(binaphtholate)	GC	198
2-Phenyl-1-butene	$(CpR)(CpR')TiCl_2(R,R' = M, NM)$	GLC, $[\alpha]_D$	151
	$C_2H_4(tH\text{-}Ind)_2Zr$-(binaphtholate)	GC	198
2-Methyl-1-pentene	$C_2H_4(tH\text{-}Ind)_2ZrMe_2$	GC	198

[a] Cocatalyst = methylaluminoxane (MAO) unless specified otherwise; [b] NMR = ^{13}C NMR spectroscopy, MW = molecular weight, DSC = differential scanning calorimetry, GC = gas chromatography, MS = mass spectrometry, IR = infrared spectroscopy; DSC = differential scanning calorimetry, XRD = X-ray diffraction analysis, $[\alpha]_D$ = optical rotation.

polymers obtained with these supported catalysts are the same as those obtained with their homogeneous analogues, but catalytic activities are reduced. This suggests that the catalyst molecules adsorb onto the support surface with their structure intact. However, the production of metal active centres via this process appears to be inefficient [182]. Table 4 shows the supported metallocene catalysts which have been used for polymerisation of ethene and propene as well as the copolymerisation of ethene with α-olefins.

7. Other catalytic applications of Group 4 metallocene complexes (Table 5)

Many other uses besides α-olefin polymerisation applications have recently been found for Group 4 metallocenes. These catalysts, in conjunction with a cocatalyst such as MAO, are able to carry out the stereospecific cyclopolymerisation of terminal dienes [183]. For example, 1,5-hexadiene is cyclopolymerised by Cp_2ZrCl_2, $Cp^*_2ZrCl_2$ [184,185] and optically active $C_2H_4(tH\text{-}Ind)_2Zr(1,1'\text{-binaphtholate})$ [186,187]. Cationic complexes such as $Cp^*_2ZrMe^+$ have also been used in this application [188]. 2-Methyl-1,5-hexadiene is also cyclopolymerised by $Cp^*_2ZrCl_2$/MAO or $Cp^*_2ZrMe^+$ [189]. *Terpolymers* of ethene, propylene and 1,5-hexadiene may be synthesised with $Et(Ind)_2ZrCl_2$ [190]. *Cycloolefin polymerisation*, without ring opening, to give isotactic, highly crystalline polymers is also accomplished by these catalysts. Cyclopentene, cyclobutene and norbornene are among the monomers polymerised by $C_2H_4(Ind)_2ZrCl_2$/MAO [74,174,191–196]. The homopolymerisation of α-olefins with silyl-protected alcohols and tertiary amines has also recently been accomplished, using $[Cp^*_2ZrMe][B(C_6F_5)_3]$ [197].

Group 4 metallocene catalysts have also been used for the *enantioselective hydrogenation of olefins*. Internal or 2- or 3-substituted terminal olefins do not undergo polymerisation but can be hydrogenated by catalysts such as optically active $C_2H_4(tH\text{-}Ind)_2Zr(1,1'\text{-binaphtholate})$ [198]. 2-Phenyl-1-butene is hydrogenated by $C_2H_4(tH\text{-}Ind)_2Zr(H)(NPhMe_2)^+$ [199] or by $(CpR)(CpR')TiCl_2/Li(H_2Al(OCH_2CH_2OMe)_2)$ (R = M, NM, R′ = H; R = R′ = M, NM) [200]. Propene and 1-butene have been hydrogenated with $C_2H_4(tH\text{-}Ind)_2Zr(bis(o\text{-acetyl-(R)-mandelate}))$/MAO [201,202]. $(CpCH(Me)(Ph)_2ZrR_2$/MAO (R = H, Me) is another good catalyst for the hydrogenation of prochiral alkenes [203]. The enantioselective reduction of C = N bonds has also been discussed [204].

The *asymmetric hydrooligomerisation of propene* can be carried out using $C_2H_4(tH\text{-}Ind)_2ZrMe_2$/MAO [205], the chloride derivative of which has also been used for 1-butene *oligomerisation* [174]. 1-Hexene [206] and 1-octene [207] have been oligomerised with Cp_2ZrCl_2/MAO. 1-Butene and 4-methyl-1-pentene may be *polymerised* with $Cp^*_2MCl_2$/MAO (M = Zr, Hf) [208]. $(CpMe_4)_2TiMe_2$ has been used as an initiator for the thermal or photochemical *isomerisation of olefins* [209].

Other applications of these catalysts include their use as hydrozirconation reagents [86], asymmetric induction in Diels–Alder reactions [210], the catalytic ethylmagnesation of homoallylic alcohols and ethers with Cp_2ZrCl_2 [211], the coupling of alkynes with Cp_2TiCl_2 [212] and the functionalisation of the methyl

TABLE 6. α-Olefin polymerisation reactions of cationic Group 4 metal alkyl complexes

Monomer	Catalyst	Polymerisation conditions				Activity/ 10^5 g polymer $(mol\ M)^{-1}h^{-1}$	Ref.
		[M]/ 10^{-3} M	T/°C	P/bar	Solvent		
Ethylene							
	M = Ti						
	$[Cp_2TiMe][BPh_4]$	21.7	−20	1	CH_2Cl_2	0.03	50,236
	$[Cp_2Ti(CH_2SiMe_3)(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	237
	$[(CpSiMe_3)_2TiMe][BPh_4]$	21.7	−20	1	CH_2Cl_2	0.04	50
	$[(CpSiMe_3)_2TiMe][B(C_6F_5)_4]$	15	0	1	CH_2Cl_2	0.5	235
	$[(CpSiMe_3)_2TiMe]$ $[B(C_6H_3(CF_3)_2)_4]$	12	0	1	CH_2Cl_2	0.4	235
		1.85	21	1	Toluene	0.8	235
	$[Me_2Si(Cp)_2Ti(CH_2SiMe_3)$ $(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	237
	$[Ind_2TiMe][BPh_4]$	18–21	−40	1	CH_2Cl_2	0.03–0.07	50,236
	M = Zr						
	$[Cp_2Zr(H)(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	225
	$[Cp_2ZrMe][BPh_4]$	—	—	1	CH_2Cl_2	—	236
	$[Cp_2ZrMe][MeB(C_6F_5)_3]$	—	25	1	Toluene	45	232
	$[Cp_2Zr(Me)(thf)[BPh_4]$	—	—	1	CH_2Cl_2	0.12	225,47,86
	$[Cp_2Zr(Ph)(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	225
	$[Cp_2Zr(CH_2Ph)][B(C_6F_5)_4]$	0.3	60	1	Toluene	11	226
	$[Cp_2Zr(CH_2Ph)][CB_{11}H_{12}]$	—	—	—	—	—	221
	$[Cp_2Zr(CH_2Ph)(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	225,296
	$[Cp_2Zr(CH_2SiMe_3)(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	237
	$[(CpMe)_2Zr(R)(thf)][BPh_4]$						
	R = H, CH_2Ph	—	—	—	CH_2Cl_2	—	239
	$[(CpSiMe_3)_2ZrMe][B(C_6F_5)_4]$	0.8–1.3	21	1	Toluene	15.4–23.3	235
	$[(CpSiMe_3)_2Zr(CH_2Ph)][B(C_6F_5)_4]$	0.3	25–60	1	Toluene	7.4–56	240
	$[(Cp\{1,2\text{-}Me_2\})_2ZrMe][MeB(C_6F_5)_3]$	—	25	1	—	—	232
	$[(CpMe_4Et)_2ZrMe][C_2B_9H_{12}]$	—	—	—	Toluene	—	231
	$[Cp^*{}_2ZrMe][MeB(C_6F_5)_3]$	—	25	1	—	—	232
	$[Cp^*{}_2ZrMe][C_2B_9H_{12}]$	0.17	40	16	Toluene	42.2	231
	$[Cp^*{}_2Zr(CH_2SiMe_3)(thf)][BPh_4]$	—	—	—	Toluene	—	237
	$[Cp^*{}_2Zr(m\text{-}C_6H_3R)][B(C_6H_4R)_3]$						
	R = H	—	—	—	Toluene	—	231,237
	R = Me	1.3	80	6	Toluene	22.5	231
	R = Et	—	—	—	Toluene	—	231
	$[C_2H_4(Ind)_2Zr(CH_2Ph)]$ $[B(C_6F_5)_4]$	0.1–0.2	25–60	1	Toluene	42–170	230
	$[me_2Si(Cp)_2Zr(CH_2SiMe_3)$ $(thf)][BPh_4]$	—	—	—	CH_2Cl_2	—	237
	$[Me_2C(Flu)(Cp)Zr(CH_2Ph)]$ $[B(C_6F_5)_4]$	0.2–0.5	0–60	1	Toluene	4.1–160	230
	M = Hf						
	$[(CpSiMe_3)_2HfMe][B(C_6F_5)_4]$	1.6–2.6	21–41	1	Toluene	7.96–12.00	235
Propylene							
	M = Zr						
	$[Cp_2ZrMe][BPh_4]$	—	0	1	CH_2Cl_2	—	236
	$[Cp_2Zr(CH_2Ph)][B(_6F_5)_4]$	0.5	60	1	Toluene	5.2	271
	$[C_2H_4(Ind)_2ZrMe][BPh_4]$	0.9	15	6	C_6H_5Br/ toluene	0.13	234
	$[C_2H_4(Ind)_2ZrMe][B(C_6F_5)_4]$	0.25–100 000	−55–24	1–1.7	Toluene	2.4–205	270,271,223
	$[C_2H_4(tH\text{-}Ind)_2ZrMe][BPh_4]$	0.85	15	6	C_6H_5Br/ toluene	0.19	234
	$[Me_2C(Cp)(Flu)Zr(CH_2Ph)]$ $[B9C_6F_5)_4]$	0.23	−20–60	1	toluene	0.5–2.0	271

C–H bonds in 2,6-lutidine and other pyridine derivatives with $Cp_2Zr(\eta^2\text{-C,N-}CH_2\{6\text{-methyl-2-pyridyl}\})^+$ [213,214]. Recently the use of binaphthyl bridged indenyl titanium complexes to induce catalytic epoxidation of alkenes has been reported. Cp_2TiCl_2 has also been shown to be effective as an antitumour agent in mice. Substitution of the ring leads to a decrease in antitumour potency, the magnitude of which depends on the degree of ring modification [215].

These and other applications of Group 4 metallocene catalysts are summarised in Table 5.

8. Cationic zirconocene catalysts (Table 6, 7)

Homogeneous catalysts, active for ethene polymerisation without a cocatalyst or support, are formed by reacting dialkylzirconocenes with an equimolar amount of a strongly acidic salt of a non-coordinating anion, *e.g.* $[Me_2PhNH]^+[B(C_6F_5)_4]^-$. Recently, a method for the preparation of these metallocenium species from the more stable metallocene dichlorides by reaction with Et_3Al and $B(C_6F_5)_4$ has been published [216]. The true active species is believed to be the Cp_2ZrMe^+ cation [217]. The synthesis, stability in solution, and reactions, of these complexes were reviewed by Jordan in 1991 [218]. The development of novel so called "non-coordinating" anions has greatly assisted in the development of this chemistry [219–224]. This brief section will concentrate on polymerisation applications and substituent effects shown by the cyclopentadienyl rings in these cations.

Cationic d^0 14-electron alkyl complexes have been implicated as the active species in metallocene-based Ziegler–Natta polymerisation systems, including the Cp_2MX_2/alumoxane catalysts. The Cp_2MR^+ complex is highly coordinatively and electronically unsaturated, facilitating olefin coordination and insertion into the M–R bond [225]. The study of these catalysts is thus important because "single-site" catalysts aid understanding of alumoxane-containing catalysts. The comprehensive characterisation of these latter complexes is hampered by the indeterminate nature of the cocatalyst [226].

Ethene polymerisation has been carried out with a variety of cationic catalysts, including $Cp_2Zr(R)(thf)^+$ ($R = CH_2Ph$ [227], Me [47,228]) and $(CpMe)_2Zr(CH_2Ph)(thf)^+$ [229], but the rates are not comparable as a result of the different reaction conditions employed. A comparison of a series of $[(CpR)_2Zr(CH_2Ph)][B(C_6F_5)_4]$ ethene polymerisation catalysts showed the following reactivity order: $(CpR)_2 = C_2H_4(Ind)_2 > Me_2C(Flu)(Cp) > (CpSiMe_3)_2 > Cp_2$ [230]. Propene polymerisation has also been performed with $C_2H_4(tH\text{-}Ind)_2ZrMe^+$, $Me_2C(Cp)(Flu)ZrMe^+$ and Cp_2ZrMe^+ [216]. Some reports on the use of substituted catalysts have also been published. Catalysis with peralkylated zirconocenes prevents anion degradation and maximises the lability of the anion to the incoming olefin, leading to higher polymerisation activities [231]. Ethene polymerisation with $(CpR)_2ZrMe^+$ complexes (CpR = CpH, Cp*, Cp{1,2-Me_2}) showed that these catalysts had activities comparable to those of Cp_2ZrCl_2/MAO [232], although the actual values were not directly comparable. This implies that the cationic systems are stoichiometrically precise models of alumoxane-based catalysts [233]. In a propene polymerisation study using $(CpR)_2ZrMe^+$ catalysts, the ${}^tBu$-substituted catalyst was more active than its Me_3Si-substituted analogue

TABLE 7. Other olefin-related reactions of cationic Group 4 metal alkyl complexes

Reaction type	Catalyst	Analyses [a]	Ref.
Copolymerisation of:			
Ethylene and propylene	$[C_2H_4(Ind)_2Zr(C_2H_5)][B(C_6F_5)_4]$	NMR	216
Terpolymerisation of:			
Ethylene, propylene and ethylidene norbornene	$[C_2H_4(Ind)_2Zr(C_2H_5)][B(C_6F_5)_4]$	NMR	216
Cyclopolymerisation of:			
1,5-Hexadiene	$[Cp^*_2ZrMe][B(C_6F_5)_4]$	—	188
2-Methyl-1,5-hexadiene	$[Cp^*_2ZrMe][B(C_6F_5)_4]$	—	291
4-(Me_3SiO)-1,6-heptadiene	$[Cp^*_2ZrMe][B(C_6F_5)_4]$	NRM, GC	197
	$[C_2H_4(tH\text{-}Ind)_2ZrMe][B(C_6F_5)_4]$	NMR, GC	197
4-(${}^tBuMe_2SiO$)-1,6-heptadiene	$[C_2H_4(tH\text{-}Ind)_2ZrMe][B(C_6F_5)_4]$	NMR, GC	197
5-${}^tBuMe_2SiO$-1-pentene	$[Cp^*_2ZrMe][B(C_6F_5)_4]$	NMR, GC	197
5-(*N*,*N*-diisopropylamino)-1-pentene	$[Cp^*_2ZrMe][B(C_6F_5)_4]$	NMR, GC	197
	$[C_2H_4(tH\text{-}Ind)_2ZrMe][B(C_6F_5)_4]$	NMR, GC	197
Oligomerisation of			
Propylene	$[(CpMe)_2Zr(CH_2Ph)][CB_{11}H_{12}]$	—	221
	$[Cp^*_2MMe(THT)][BPh_4]$, M = Zr, Hf	—	185
3,3-Dimethyl-1-butyne	$[Cp^*_2ZrMe][B(C_6H_4F)_4]$	NMR	297

[a] NMR = nuclear magnetic resonance spectroscopy, GC = gas chromatography.

[234]. Terminal alkynes were noted to undergo reactions with $(CpR)_2ZrMe^+$ complexes ($CpR = Cp^*$, Cp^tBu, $CpSiMe_3$; $(CpR)_2 = C_2H_4(Ind)_2$). The alkynes were rapidly and regioselectively oligomerised to dimers and trimers when the pentamethyl-substituted compound was used. However, the less sterically hindered compounds showed no oligomerisation activity due to the formation of inactive dimetalloalkene complexes [107]. From so few results, trends in substituent effects are not clear, but electron-donating substituents would appear to stabilise the cation and thus increase its polymerisation activity.

In several studies which compared the relative activities of Ti, Zr and Hf cationic catalysts, the reactivity order was found to be Zr > Hf ≫ Ti. The Zr catalysts were also thermally the most stable catalysts [235–237].

9. Lanthanide metallocene catalysts

These catalysts deserve mention since they are analogues of the Cp_2MR^+ d^0 Group 4 metallocene catalysts. The insight into mechanistic aspects of polymerisation given by these complexes is important since intermediates can be isolated more easily than in the case of the Ti, Zr and Hf metallocenes [80,238–241].

Among the cyclopentadienyl-substituted catalysts used in these studies is Cp_2^*ScR (R = Me, Et, ^{i}Pr), which inserts ethene at −80°C [80]. The reaction of $(CpMe_3)_2ThMe_2$ with $[^nBu_2NH][B(C_6F_5)_4]$ produced a catalyst which was active for ethene polymerisation [242], whereas its Cp* analogue was only marginally active [231] $[(CpMe_4)Me_2Si(\eta^1\text{-}NCMe_3)](PMe_3)ScH]_2$ catalysed the regiospecific polymerisation of propene, 1-butene and 1-pentene up to a degree of polymerisation of 70 [243]. Finally, studies on *rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}^tBu\text{-}Cp)_2Y(\mu\text{-}H)_2$ revealed that it polymerised propene, 1-butene, 1-pentene and 1-hexene to modest MW polymers [244].

10. Conclusion

It is clear from the above discussion that the influence of the ring substituent in $(CpR)_2MCl_2$ complexes on α-olefin polymerisation reactions is substantial. The numerous reports in which the R group has been varied have led to detectable changes in catalyst activity and polymer characteristics. This has been clearly indicated by the remarkable influence observed on polymer tacticity when propene is polymerized in the presence of bridged metallocene catalysts. Indeed the intensive investigations of these metallocene polymers has led to one of the few recent examples in which organometallic complexes will be used in a bulk industrial process. Notwithstanding the detectable achievements that have been made, the relationship between catalyst structure and polymer yield and properties has not been clearly identified. (The recent molecular modelling results may guide an understanding of this relationship.) A summary of the situation is given below:

(a) Very few comparative studies for a series of related metallocene complexes have been reported. Since most researchers use different reaction conditions, comparisons between different studies is generally not possible.

(b) In most studies, no attempt has been made to relate the effect of minor changes on the catalyst at the molecular level to polymer properties. For example, the role of electronic and steric effects are described in qualitative rather than quantitative terms. (Procedures to quantify both the steric and electronic effects are available.)

(c) Since the structures of the alumoxanes are not known with certainty their role in the catalytic reaction is not known explicitly. Procedures to use metallocene cations in the absence of alumoxanes are thus preferred for mechanistic studies. Very few comparative studies using these cationic systems, in which the cyclopentadienyl ring substituents are varied, have to date, been reported.

(d) Point (b) above could be responsible for the observation of inconsistencies in comparative studies which have been reported in the literature.

(e) Some general conclusions that can be drawn from the reports available in the literature on $(CpR)_2MCl_2$ catalysts are (i) electronic effects associated with R dominate, with electron donating groups giving, in general, enhanced catalyst activity; (ii) steric effects play a more minor role, provided access to the metal by reagent is possible. However, a steric threshold exists in these systems and if large α-olefins or a small metal ion (Ti versus Zr) are used then catalyst activity will be dominated by steric effects.

(f) Steric effects should play a dominant role in the determination of polymer tacticity (enantiomorphic or end chain control). Methods to quantify and hence control tacticity still need to be developed.

From the above it is apparent that although much is known about the new metallocene polymerisation catalysts numerous research avenues which will lead to a deeper understanding of the catalyst and its properties remain to be explored.

11. Abbreviations

Cp	cyclopentadienyl ligand ($\eta^5\text{-}C_5H_5$)
Cp′	methylcyclopentadienyl ligand ($\eta^5\text{-}C_5H_4Me$)

Cp*	pentamethylcyclopentadienyl ligand (η^5-C_5Me_5)
EAO	ethyl alumoxane
EPDM	ethylene, propene, diene monomers
LLDPE	linear low density polyethylene
MAO	methyl alumoxane
MW	molecular weight
MWD	molecular weight distribution
PE	polyethylene
PP	polypropylene

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