

Group 4 metal complexes for homogeneous olefin polymerisation: a short tutorial review

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Abstract The discovery of transition metal-catalysed polymerisation of olefins in the 1950s by Ziegler and Natta was of huge importance. Over the last 30 years, the interest in homogenous polymerisation has not only grown but has changed focus from primarily studying the metallocene complexes of Group 4 to widespread exploration of post-metallocene systems. This is a consequence of extensive patenting of the metallocene catalyst systems, as well as for general interest in the improvement of polyolefin catalysis. The plastics industry produces more than 10^7 tonnes of polyethylene, polypropylene and polystyrene each year worldwide, and the study of well-defined homogenous catalysts is invaluable in uncovering the mechanism of polymerisation and the fundamental properties of the active species. This short Tutorial Review gives an overview of homogenous transition metal Ziegler–Natta catalysis in general as well as an overview of a selection of Group 4 post-metallocene catalysts. An overview of the synthesis and reactions of alkyl cations relevant to olefin polymerisation is also given. Finally, this review summarises recent advances in bimetallic catalysts for olefin polymerisation.

Keywords Olefin polymerisation · Catalysis · Bimetallic catalysis · Alkyl cations

Introduction to Ziegler–Natta catalysis

Ziegler and Natta were awarded the Nobel Prize in Chemistry in 1963 “for their discoveries in the field of the chemistry and technology of high polymers”. Ziegler and Natta [1–3] discovered that heterogeneous polymerisation of ethylene and propylene could be achieved by mixtures of transition metal and trialkylaluminium compounds; such systems included $\text{TiCl}_4/\text{AlEt}_3$. To this day, the majority of industrially produced polyolefins are produced in this way. These systems have been widely developed over the last 50 years and act as efficient and selective catalysts for many types of olefin polymerisation. The main problem with these catalysts is the lack of definition in the active site. Without a well-defined active site, rational catalyst design and characterisation is difficult, and the polymer produced by such a system has a broad molecular weight distribution. This is where the study of homogenous catalysis finds its benefits. The molecules which now act as the active sites for catalysis can be completely defined and characterised by methods such as NMR spectroscopy or X-ray crystallography with relative ease leading to logical catalyst design. This short tutorial review, focussing on Group 4 metals and metallocene and half-sandwich types of compounds in particular, is not intended by any means to provide an exhaustive account of the literature. The reader is directed to several review articles for a more comprehensive overview of homogenous Ziegler–Natta catalysis [4–14].

Metallocene catalysts

Sir Geoffrey Wilkinson [15], who won a Nobel prize in 1973 together with Ernst Otto Fischer “for their pioneering work, performed independently, on the chemistry of the

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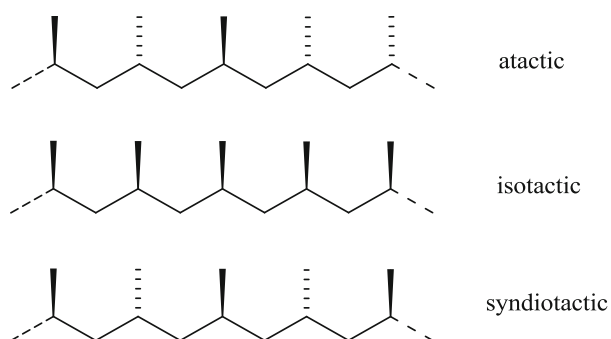


Fig. 1 The main types of tacticity in polypropylene

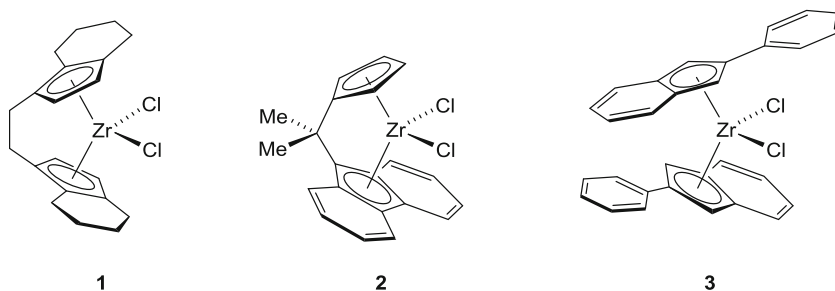
organometallic, so called sandwich compounds”, reported the syntheses of Cp_2TiBr_2 and Cp_2ZrBr_2 in 1953. In 1957, Natta and Breslow [16, 17] both reported that the bent metallocene Cp_2TiCl_2 in conjunction with Et_2AlCl or AlEt_3 could polymerise ethylene but not propylene. This system was not ideal, however, as the polymerisation was slow. Unexpectedly in 1980, Sinn and Kaminsky [18–20] discovered that addition of a small amount of water to metallocene/alkylaluminum systems vastly increased the system’s polymerisation activity. This was due to the formation of methyl aluminoxane (MAO) which is formed from the partial hydrolysis of trimethylaluminum (TMA) and can be prepared prior to polymerisation or in situ. MAO can be used in general to activate a variety of Group 4 metallocenes towards ethylene or α -olefin polymerisation [21, 22].

Metallocene systems activated with MAO are also capable of polymerising propylene. One such system is the zirconocene system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$. An extra consideration when polymerising propylene, due to the presence of an extra methyl group per monomer, is tacticity. This is defined by the relative chiral arrangement of adjacent pendant methyl groups. Examples of the principal different stereochemistry possible in polypropylene can be seen in Fig. 1.

Constrained geometry catalysts (CGCs) and *ansa*-metallocenes

Following the discovery of metallocene catalysts, the 1980s saw a considerable amount of research into catalysts that could control the stereochemistry and thus

Fig. 2 *Ansa*-metallocene catalysts which can control the tacticity of polypropylene



microstructure of the resulting polyolefin. Variation of metallocene symmetry (see Fig. 2 for examples) was discovered to be the main factor in determining the tacticity of the final polymer [10].

The ligand sets investigated were metallocene based, but the two supporting ligands were linked by an *ansa*-bridging moiety. This connection prevents rotation of the ligands helping to well define the steric environment of the active site. Kaminsky and Brintzinger [23] developed the C_2 symmetric zirconocene catalyst **1** which produced highly isotactic polypropylene; the sterics defined in the active site control the insertion of each monomer to give this microstructure. Ewen et al. [24] later found that C_s symmetric complex **2** produced highly syndiotactic polypropylene. Although it is not an *ansa* compound, in 1995, Coates and Waymouth [25] described a sterically crowded metallocene compound **3** which acted in a similar fashion; although this was not constrained by a physical bridge, the bulky groups led to restricted rotation. In the absence of a physical link, the top and bottom ligands could rotate intermittently, and thus, the catalyst fluctuates between chiral and achiral producing a block polymer containing isotactic and atactic sections.

Limited thermal stability and the production of low molecular weight polymers under commercially relevant conditions by the metallocene *ansa*-catalysts resulted in the development of a new catalyst type, the constrained geometry catalysts (CGCs) [10, 26]. Steven et al. [26, 27] define a CGC as “a complex in which a π -bonded moiety is linked to one of the other ligands on the same metal centre in such a way that the angle measured between the centroid of the π -system and the additional ligand is smaller than the comparable unbridged complex”. This important class of catalyst was developed by Dow [26–30] and Exxon [31–34] following the discoveries of silane-bridged cyclopentadienyl-amido scandium and titanium catalysts by Bercau and Okuda [35, 36], respectively. The general form of a CGC is illustrated in Fig. 3.

CGC catalysts have outstanding performance in ethylene polymerisation and in copolymerisations with higher α -olefins. The reasons for superior performance in these areas compared with metallocenes are a more open coordination sphere, a small $\text{Cp}_{\text{cent}}\text{-M-N}$ angle and a reduced

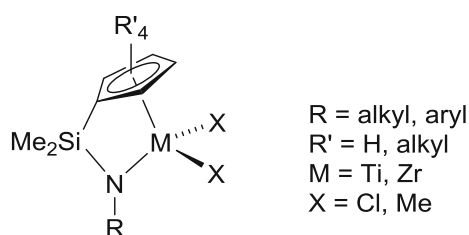


Fig. 3 General form of a constrained geometry catalyst (CGC)

propensity to undergo chain transfer [26]. The amido group acts as a maximum three-electron donor, *cf.* cyclopentadienyl (five-electron donor), which yields a highly electrophilic metal centre and thus results in its high productivity as a catalyst. CGCs can be used in high-temperature polymerisation processes because of their high thermal stability and ability to produce higher molecular weight polymers than their metallocene counterparts [37, 38].

Post-metallocene catalysts and the isolobal analogy

Due in part to extensive patenting of the more traditional Group 4 metallocene systems and CGCs, new post-metallocene systems were of great research interest during the 1990s and onwards [9, 11]. Research efforts directed at new types of catalysts also allowed for a chance to improve and control resultant polymer properties and to explore new monomer combinations. Post-metallocene systems aim to replace one or more of the cyclopentadienyl ligands on the metal centre with a different moiety. A strategy that has been successfully employed in new ligand design is the isolobal analogy developed by Hoffman [39] for which he was awarded a Nobel prize alongside Fukui “for their theories, developed independently, concerning the course of chemical reactions”. When two electronically defined systems are isolobal with each other, the symmetry, shape and energies of the frontier orbitals are similar. This principle, when combined with the correct steric properties, can be powerful in ligand design for new catalysts.

Ligands relevant to this project, which have been employed because they fulfil the criteria put forward by the isolobal analogy, consist of an anionic heteroatom binding to the metal centre in a κ^1 -mode. If one considers the cyclopentadienide ligand and compares its electronic properties to the general form of a κ^1 -bound anionic donor, for example, an imido ligand, the isolobal analogy can be seen in operation (see Fig. 4). The frontier orbitals of each ligand comprise a single σ -donor and two π -donor orbitals which can interact with the metal centre.

Previous work in the Mountford group has utilised this analogy in the synthesis of titanium imido compounds such as $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}_2$ (**4**, $\text{Me}_3[9]\text{aneN}_3 = 1,4,7$ -

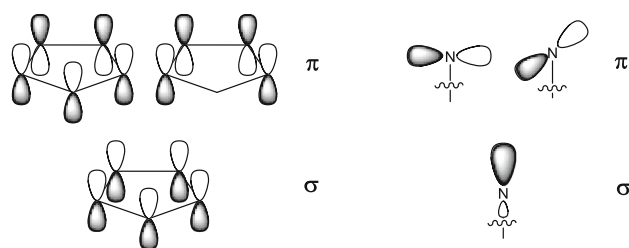
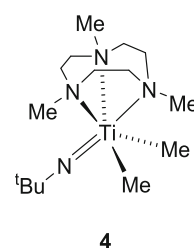


Fig. 4 Occupied frontier orbitals of cyclopentadienide and NR^{2-} ligands

trimethyl triazacyclononane) or related compounds [13, 40–43]. In this compound, the $[\text{NR}]^{2-}$ ligand is isolobal with Cp^- , but since it is formally dianionic, the other supporting ligand, for example, a 1,4,7-triazacyclononane, must be neutral to keep the charges balanced in the compound. DFT calculations show that the frontier molecular orbitals of dicationic imido species $[\text{Ti}(\text{NMe})(\text{H}_3[9]\text{aneN}_3)]^{2+}$ ($\text{H}_3[9]\text{aneN}_3 = 1,4,7$ -triazacyclononane) are broadly similar to that of $[\text{Cp}_2\text{Ti}]^{2+}$ in line with the isolobal analogy [44]. For in-depth computational studies on $[\text{Cp}_2\text{M}]^{n+}$, the reader is directed to a detailed review article [45].

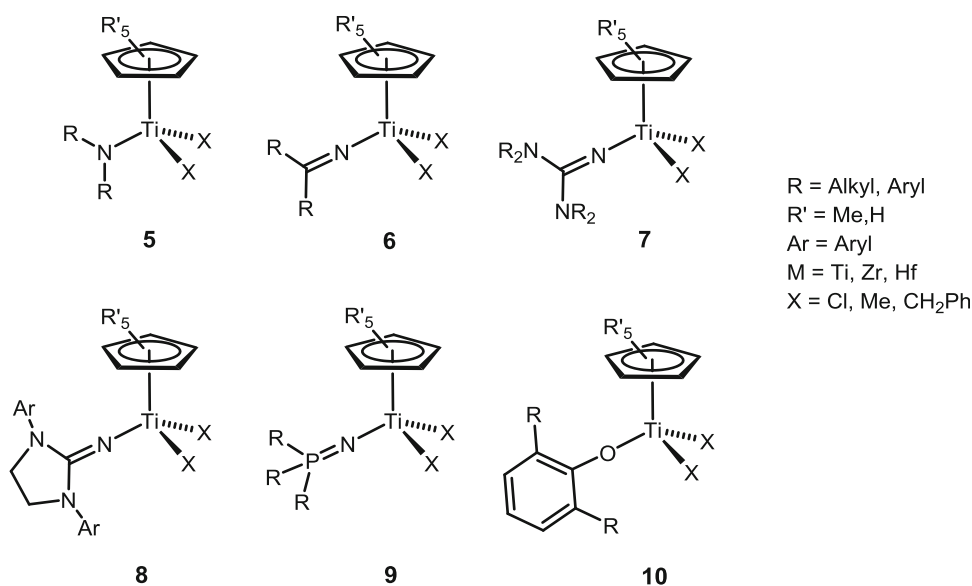


Non-CGC half-sandwich catalysts

Group 4 complexes of the form $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{L})\text{X}_2$ ($\text{M} = \text{Group 4 metal}$, $\text{L} = \text{supporting ligand}$, $\text{X} = \text{halide or alkyl}$), which are supported by one cyclopentadienyl and one κ^1 -bound formally monoanionic ligand, have been well studied [9, 11, 46]. The monoanionic ligands act as an isolobal analogue of cyclopentadienide and also possess the same charge; thus, they can be directly substituted without the need to change the other supporting ligand. Prominent examples comprise amide (**5**) [47–49]-, ketimide (**6**) [50–54]-, guanidinate (**7**) [55]-, iminoimidazolidide (**8**) [56–61]-, phosphinimide (**9**) [62–70]- and aryloxide (**10**) [71–76]-supported half-sandwich compounds (Fig. 5). The κ^1 -bound N-donor ligands will be discussed further below.

The first half-sandwich ketimide complex of the form $\text{Cp}^R\text{M}(\text{NCR}_2)\text{Cl}_2$ ($\text{Cp}^R = \text{C}_5\text{R}'_5$, $\text{R}' = \text{H or alkyl}$, $\text{R} = \text{alkyl}$) was reported in 1986 by Leigh et al. [77], namely $\text{CpTi}\{\text{NC}(\text{tBu})\text{tBu}\}\text{Cl}_2$. Since then, a large number of compounds of this type have been reported, and the area has been reviewed [54]. In $\text{CpTi}\{\text{NC}(\text{tBu})\text{tBu}\}\text{Cl}_2$, the

Fig. 5 Half-sandwich post-metallocene precatalysts



coordination of the ketimide to the metal is approximately linear [Ti–N–C, 171.3(4)°] indicating that the nitrogen atom is effectively *sp* hybridised and suggests the possibility of Ti–N multiple bonding. Another important system where the ketimide-supporting ligand is –NC^tBu₂ was reported by Dias, Nomura and Zhang [50, 52, 53, 78]. However it was over a decade between the first reported synthesis of the half-sandwich ketimide complexes and their recognition as polyolefin catalysts.

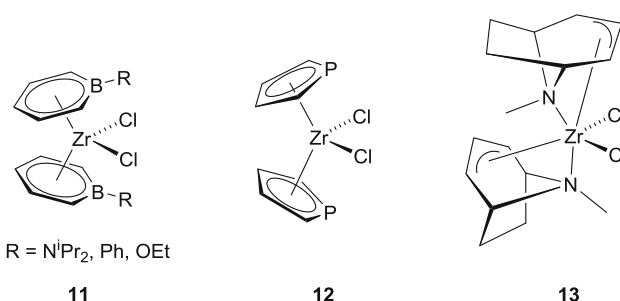
Another important and comprehensively studied ligand is phosphinimide (**9**, –NPR₃, R = alkyl or aryl). Stephan et al. [63] have investigated CpTi(NPR₃)X₂ (R = alkyl or aryl, X = halide or alkyl) complexes since the 1990s regarding their general reactivity and polymerisation ability. Phosphinimide ligands have been shown to bind in a linear fashion to the metal centre with a short M–N bond [69, 70]. These attributes are evidence of a $\sigma+2\pi$ -bonding mode between ligand and metal just like Cp. The steric influence of the phosphinimides have also been shown to be comparable with Cp, and it is argued that the steric influence of the ligand is the most important factor in determining the polymerisation activity in these particular systems [65, 67].

The steric influence of the ligand is also thought to be important in aryloxyde-supported half-sandwich systems (**10**), but in others it appears to be the electronic effects that are considered key to catalyst productivity. Hessen [57], Tamm [59, 60] and Nomura [58] have all investigated iminoimidazolidide ligands (cyclic guaninates, **8**, Fig. 5), and it has been suggested that an increase in π -bonding between the ligand and titanium can lead to an increase in catalytic activity [57–60]. The significant π -bonding in these complexes originates from formal lone pair donation of the amino nitrogens towards the π_{CN} system, which means the ligand can be considered up to a five-electron donor via a $\sigma+2\pi$ interaction

(Fig. 6). This electronic arrangement is supported experimentally by short Ti–N bond lengths and linear Ti–N–C angles. The activity of complex CpTi{NC(N(Xyl)CH₂)₂}Bn₂ is higher than ketimide-supported CpTi(NC^tBu₂)Bn₂ (1600 and 1128 kg mol^{–1} h^{–1} bar^{–1}, respectively) due to the addition of amino nitrogen donors [57].

Other Group 4 post-metallocene catalysts

Many post-metallocene catalysts have also been developed, which do not contain a cyclopentadienyl-supporting ligand [9, 11]. In some instances, they have contained ligands that still aim to imitate Cp, for example, boratobenzene [79–81]- and phosphacyclopentadienyl [82]-supported catalysts **11** and **12**.



Boratobenzenes are formed by the addition of a boron atom into a cyclopentadienide ring. Since boron contributes only an empty *p*-orbital to the π system, the aromaticity is not disturbed. When activated with MAO, the catalysts give reasonably high activities (105 kg mol^{–1} h^{–1} bar^{–1}) [79]. When changing the NⁱPr₂ substituent on boron (**11**) to less sterically demanding substituents Ph or OEt, there is an increased rate of β -hydrogen elimination resulting in more

Fig. 6 Metal–ligand bonding interactions for guanidinate-supported complexes (7)

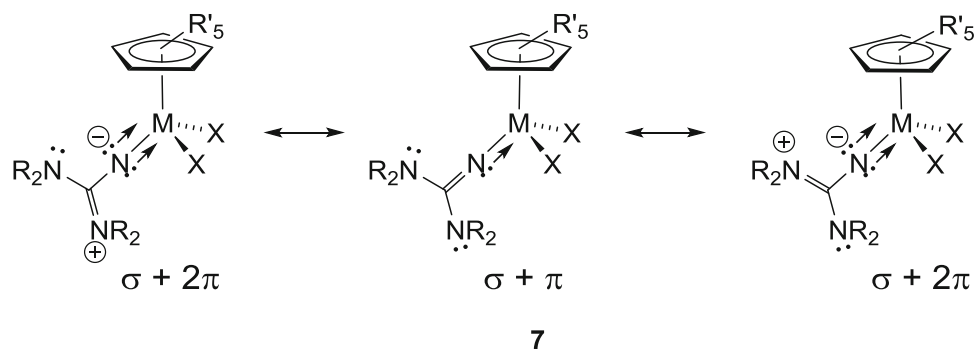
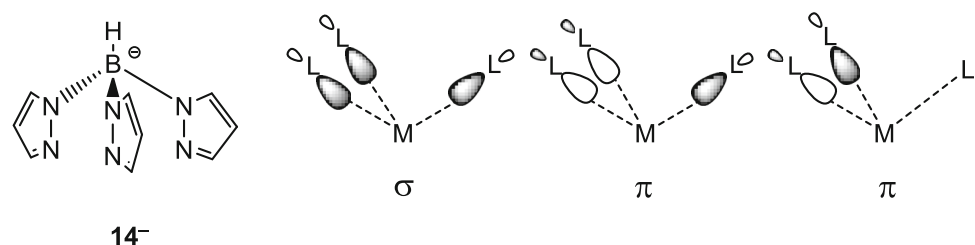


Fig. 7 [Tp][−] ligand shown alongside donor orbitals of σ - and π -symmetries for a *fac*-L₃ moiety



α -olefin production [79–81]. Phosphacyclopentadienes are obtained by the exchange of a single carbon in a cyclopentadiene ring by a P atom; this maintains the same ring size as that of Cp, as well as the aromaticity. Catalysts supported by these ligands can give productivities similar to their Cp analogues. Tropicidyl ligands have been utilised by Bergman et al. [83] as a Cp mimic in complexes such as **13** despite having separate σ and π systems. An alternative ligand that can be used in place of Cp is the monoanionic tris(pyrazol)borate (Tp) [84–86]. Although this is a face-capping ligand, it is isolobal with Cp[−]; the relevant σ - and π -orbitals are shown alongside the ligand (**14**[−]) in Fig. 7.

These ligands have been used in the Mountford group as Cp surrogates in production of Group 4 polymerisation catalysts that are supported by Tp and κ^1 -amidinate ligands [87, 88]. Other Tp-supported Group 4 polyolefin catalysts have also been investigated by other groups [89–92]. In addition, Group 4 non-cyclopentadienyl catalysts supported by κ^2N,N' -amidinate ligands have also been reported [93–96].

Metalocene and post-metallocene alkyl cations

It is generally acknowledged that the active species in Group 4-based olefin polymerisation catalysis is of the form $[L_nMR]^+$ (L = supporting ligands, M = Group 4 metal, R = alkyl group). The nature of the active species is of great importance in the fundamental understanding of the mechanism of olefin polymerisation. Once one understands the mechanisms, deactivation reactions and structure–activity relationships, then, in principle, better catalysts can be designed. This section will present a

concise introduction into the area of cationic Group 4 metal alkyl complexes and their reactivities. This subject area has been extensively reviewed [4, 8, 97, 98].

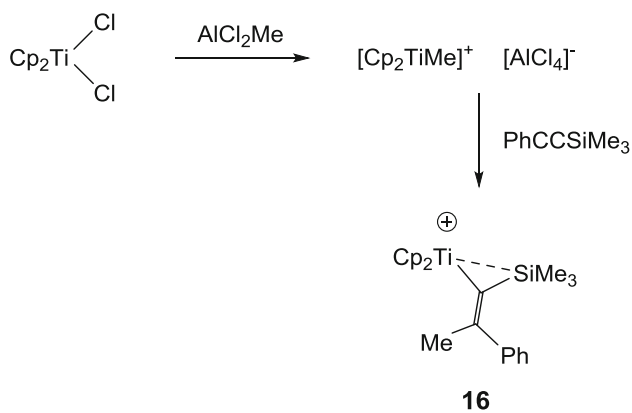
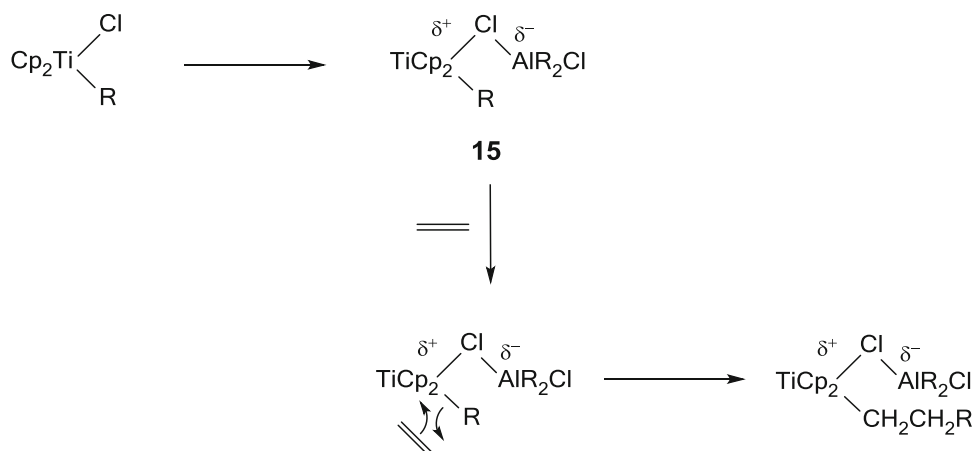
Historical background

The suggestion of a cationic active species in olefin catalysis occurred not long after initial reports of the polymerisation activity of $TiCl_4/AlEt_3$ by Ziegler in 1953. Newburg, Long and Breslow [99, 100] suggested that the active agent was a highly polarised bimetallic species (**15**) containing Ti and Al bridged by chlorine (Scheme 1).

Conductivity and electroanalysis studies by Shilov et al. [101, 102] suggested that the catalytically active species in polymerisations is actually cationic. Direct evidence for the involvement of a cationic active species was provided by electrochemical synthesis of $[Cp_2TiMe]^+$ in CH_2Cl_2 carried out by Dyachovskii [103]: polymerisation only occurred only in the cathode chamber. The idea of an ionic active species in a process which was carried out in non-polar solvents was not well accepted at the time. Curiosity was revitalised in 1985 when Eisch et al. [104] provided chemical evidence for the existence of a cationic active species by isolating $[Cp_2Ti\{Me_3SiCC(Ph)Me\}][AlCl_4]$ (**16**); this was synthesised by the insertion of the alkyne $PhCCSiMe_3$ into the then postulated $[Cp_2TiMe]^+$ (Scheme 2). This type of reaction models the insertion of ethylene into the Ti–C bond.

In 1986, both Bochmann and Jordan made important contributions in this area. Jordan et al. [105] reported the synthesis of $[Cp_2ZrMe(THF)][BPh_4]$ (**17**) which was structurally characterised and was able to polymerise ethylene. This was the first time that Group 4 cations were

Scheme 1 Insertion of ethylene into a highly polarised heterobimetallic species (15)



Scheme 2 The first example of an isolable insertion product (16) formed by insertion into the Ti–C bond of a titanium methyl cation

shown to polymerise ethylene without alkyl aluminium cocatalysts. Bochmann et al. [106, 107] reported titanocene analogues in the same year, $[\text{Cp}_2\text{TiMe(L)}][\text{X}]$ ($\text{L} = \text{NH}_3$, NCR, pyridine, $\text{X} = \text{BPh}_4$, PF_6); however, the presence of the stronger Lewis bases meant that these complexes showed no activity towards ethylene polymerisation.

Preparation of Group 4 alkyl cations

The possibility of performing polymerisation in the absence of MAO combined with the potential to undertake mechanistic investigations has led to a large amount of research into the different methods of preparing monoalkyl cations. There are a number of general synthetic routes to Group 4 alkyl cations which have been reviewed and will be discussed below [97].

Protonolysis

Ammonium salts have been used to generate alkyl cations via protonolysis of M–R bonds; an example of this is the generation of $[\text{Cp}_2\text{TiMe}(\text{NH}_3)][\text{PF}_6]$ from Cp_2TiMe_2 and

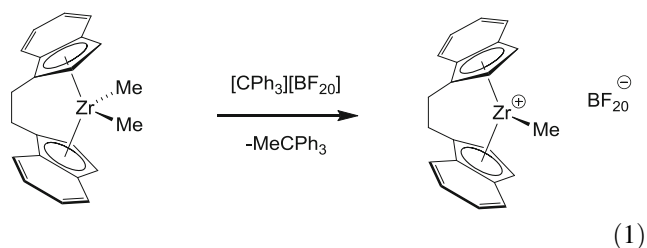
$[\text{NH}_4][\text{PF}_6]$ reported by Bochmann et al. [106]. Other ammonium salts have been used to this effect such as $[\text{PhNMe}_2\text{H}]^+$ and $[\text{tBu}_3\text{NH}]^+$. Treatment of Cp_2ZrMe_2 with $[\text{PhNMe}_2\text{H}][\text{BF}_2\text{O}]$ ($[\text{BF}_2\text{O}]^- = [\text{B}(\text{C}_6\text{F}_5)_4]^-$) produces the cation $[\text{Cp}_2\text{ZrMe}]^+$ with a $[\text{BF}_2\text{O}]^-$ counterion [97, 108]. Using protonolysis to generate the alkyl cation leads to the generation of a Lewis base side product which can bind to the cation. The Lewis base must be removed from the cation to allow binding of the olefin for polymerisation, and therefore the presence of Lewis bases reduces catalytic activity. As an alternative to ammonium salts, phosphonium salts can be used in the same vein [109]. If one employs bulky phosphonium ions such as $[\text{Cy}_3\text{PH}]^+$ and $[\text{Mes}_3\text{PH}]^+$, the resulting phosphine does not coordinate to the generated cation which then leads to a productive catalytic system [109].

Lewis acids

Tris(pentafluorophenyl)borane (“ BF_5 ”) is a strong Lewis acid and as such can be used for the activation of Group 4 alkyl-based olefin polymerisation precatalysts. This was employed by Marks et al. [110] in 1991 to synthesise $[\{1,2\text{-(CH}_3)_2\text{C}_5\text{H}_3\}_2\text{ZrMe}][\text{MeBF}_5]$ (18) which was the first example of an isolable and crystallographically characterised cation-like “Lewis base-free” species. Activating in this fashion leads to no side products that could interfere with the cation; on the other hand, the anion itself ($[\text{MeBF}_5]^-$) is known to interact with the cation. If there is an interaction, the complex is best considered as a zwitterionic molecule containing a methyl bridge between the metal and boron. The extent of interaction between the anion and the cation can be determined by the separation of the *meta* and *para* ^{19}F NMR chemical shifts [111]. This type of interaction is important to consider since it can obstruct close approach of an olefin monomer to the metal centre during polymerisation, and therefore generally, the presence of this anion leads to an inhibitory effect on the polymerisation.

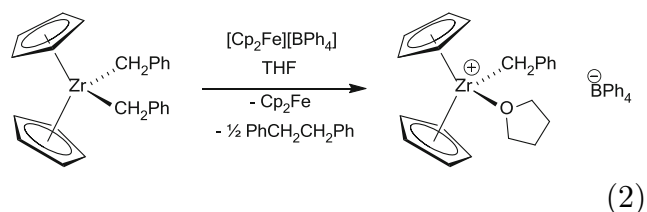
Alkyl abstraction

The most commonly employed agent used to abstract methyl groups is the trityl cation, $[\text{Ph}_3\text{C}]^+$. Abstraction of the alkyl group (R) from the precatalyst yields the formation of Ph_3CR alongside the corresponding cation [97]. This method of activation is extremely widespread, and Eq. 1 shows activation of *rac*-ethylenebis(indenyl)dimethylzirconium by way of example. If the trityl cation is coupled with an anion such as tetrakis(pentafluorophenyl)borate ($[\text{BF}_4]^-$), the product is a cation accompanied by a non-interacting anion, which acts as highly active polymerisation catalyst.

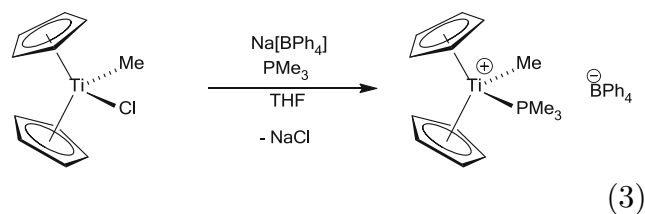


Other methods

Early methods of producing cations involved oxidative reagents such as $[\text{Cp}_2\text{Fe}]^+$ (Eq. 2) or Ag^+ [112]. Activation of dimethyl zirconocene was carried out by Jordan et al. [113] in 1986 with $\text{Ag}[\text{BPh}_4]$ yielding ethane and silver metal as side products, which occurred via oxidative cleavage of the $\text{Zr}-\text{Me}$ bond. The titanium(III) species Cp^*_2TiMe has also been shown to be oxidised by AgBPh_4 in THF to yield the monoalkyl titanocenium(IV); this process occurs via a one-electron oxidation [114].



Another method employed to generate cations is displacement of chloride by strong neutral donors, e.g. PMe_3 in complexes such as $\text{Cp}_2\text{TiMe}(\text{Cl})$ and $\text{Ind}_2\text{TiMe}(\text{Cl})$ as shown in Eq. 3.



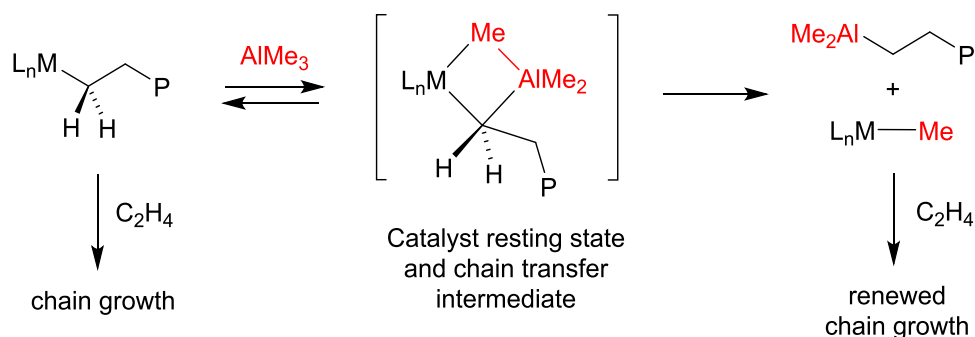
AlMe_3 and its effects on alkyl cations and polymerisation

The alkyl aluminium compound Al_2Me_6 (from now on referred to as AlMe_3) is present in polymerisation reactions that use MAO as a co-catalyst. Although this can help the process by scavenging oxygen and water from the reaction, it can also cause complications. For example, AlMe_3 can cause variation in catalytic productivity and also changes in the properties of the polymer [115–117]. Activation of zirconocene complexes with AlMe_3 can lead to a small amount of activity but are significantly less productive than their MAO-activated analogues [118]. The presence of AlMe_3 leads to the formation of heterobimetallic species of the type $[\text{L}_n\text{M}(\mu\text{-Me}_2)\text{AlMe}_2]^+$ ($\text{M} = \text{Group 4 metal}$, $\text{L} = \text{supporting ligands}$), which themselves are not catalytically active, and result in chain transfer and can also act to deactivate the active species; they are also considered to be catalytic resting states [8, 119, 120]. Alkyl aluminium compounds can also have a negative effect on the polymerisation performance of Group 4 catalysts by acting as reducing agents; titanium(III) compounds are not electrophilic enough to achieve high polymerisation activities. The more the AlMe_3 is present in solution the more the polymerisation inactive heterobimetallic species will be present. Scheme 3 illustrates the relevant processes.

The first adduct of AlMe_3 with a Group 4 alkyl cation was reported in 1994 by Bochmann et al. ($[\text{Cp}_2\text{Zr}(\mu\text{-Me}_2)\text{AlMe}_2]^+$, **19**, Fig. 8). However, this was not structurally characterised [121]. In 2006, Mountford et al. [122] reported the first cationic transition metal compound containing a $\text{M}(\mu\text{-Me}_2)\text{AlMe}_2$ moiety characterised by X-ray crystallography (**20**, Fig. 8).

To reduce the effect of AlMe_3 on the polymerisation process, scavengers can be added; one such scavenger is 2,6-di-*tert*-butyl-4-methylphenol which is more commonly referred to as butylated hydroxytoluene (BHT-H). This phenol reacts with AlMe_3 to produce $(\text{BHT})_2\text{AlMe}$ [123] which does not interfere with the active site but can still scavenge unwanted impurities [124, 125].

Scheme 3 Illustration of propagation, catalyst resting state and chain transfer to aluminium in MAO-activated ethylene polymerisation catalysis. L_nM represents a generic metal–ligand fragment; P represents a growing polymeryl chain



Anion and solvent interactions

Interaction of the anion with the cation is important to consider as it can have a substantial effect on the polymerisation process. These types of interaction occur because of a low number of valence electrons at the metal centre. If a significant interaction exists between the anion and cation, and the active site is blocked, the anion must be removed from the active site before polymerisation can take place [126] which has been shown in various metallocene and post-metallocene systems to involve quite substantial energies [127–129]. It has already been discussed above that $[\text{MeBF}_{15}]^-$ forms a strong interaction with the cationic metal centre to form a zwitterionic molecule. Equally if the anion reacts with the cation to give a different non-active species, then this too has to be circumvented by the use of a different anion. It is also worth noting that anions that are usually considered non-coordinating such as $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ have been shown to react with $[\text{Cp}_2\text{MR}]^+$, e.g. reaction of $[\text{Cp}_2\text{ZrMe}(\text{CH}_3\text{CN})]^+$ with $[\text{PF}_6]^-$ produces Cp_2ZrMeF via fluoride abstraction [113]. Even anions such as $[\text{BPh}_4]^-$ have been shown to interact with the cationic centres. Treatment of ZrBn_4 ($\text{Bn} = \text{CH}_2\text{Ph}$) with dimethylanilinium tetraphenylborate leads to the formation of $[\text{ZrBn}_3(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]$ (**21**) in which the cationic centre is stabilised by the anion. This type of interaction has also been demonstrated with $\{\text{C}_2\text{H}_4(\text{Ind})_2\}\text{ZrMe}_2$ [130]. Hlatky and Turner [108] reported that $[\text{BPh}_4]^-$ can even react with cationic species such as $[\text{Cp}^*\text{ZrMe}]^+$ to form **22** which is formed as a result of C–H activation.

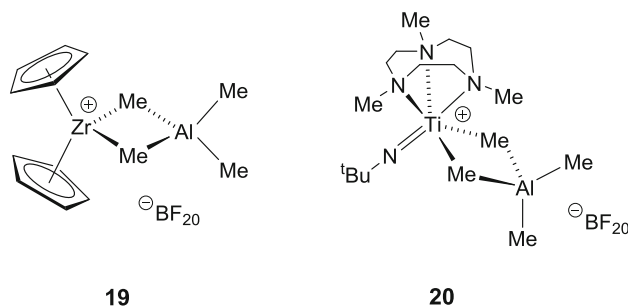
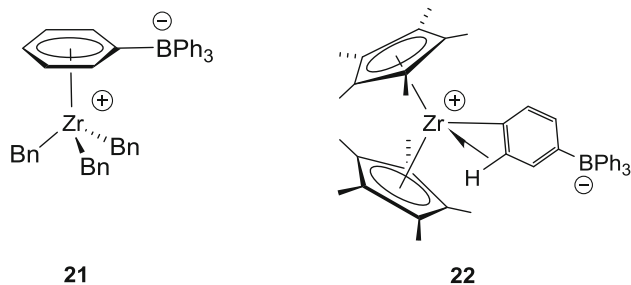
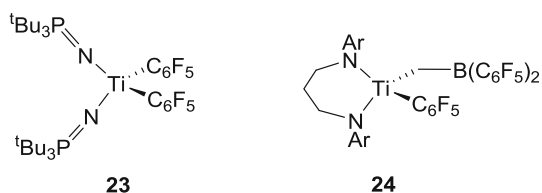


Fig. 8 AlMe_3 adducts of alkyl cations [121, 122]

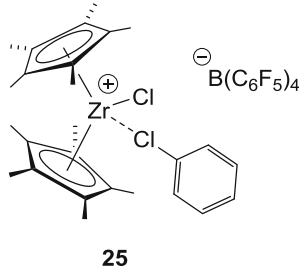
In a search of non-interacting and non-coordinating anions perfluorinated species, the most popular of which is $[\text{BF}_{20}]^-$, were investigated [130–132]. Indeed in some cases, it has been shown that a molecule of solvent would rather bind to the vacant site of the cation than $[\text{BF}_{20}]^-$; this is a testament to the anion's non-coordinating nature [133–135]. Despite its weakly coordinating nature, there have been reports of reactivity with $[\text{BF}_{20}]^-$, for example, by McConville and Stephan [64, 136] yielding **23** and **24**, respectively. Compound **23** was formed by the extraction of C_6F_5^- from $[\text{BF}_{20}]^-$ by $[(\text{tBu}_3\text{PN})_3\text{Ti}]^+$ followed by phosphinimide ligand abstraction and B–C bond cleavage.



Work by Brintzinger and Geyer in 1999 showed that, using Pulsed Gradient Spin Echo (PGSE) NMR spectroscopy, the compound $[\text{Cp}_2\text{ZrMe}][\text{BF}_{20}]$ exists as a dimer in C_6D_6 —in this case, an ion quadruple. Thus, the weakly coordinated anion $[\text{BF}_{20}]^-$ can interact with cations sufficiently to form higher aggregates [137]. Marks et al. [138] reported using similar PGSE NMR measurements in C_6D_6 that $[\text{Cp}^*\text{ThMe}][\text{BF}_{20}]$ exists as only monomeric tight ion pairs. PGSE reveals that PPh_3 , THF, benzene and toluene adducts of various zirconocene type systems can exist as ion

quadruples or even hexuples in solution at higher concentrations. It is worth noting that the previously mentioned PGSE NMR experiments were carried out at concentrations above that which is usually used in single-site catalysis, and the existence of these aggregates at lower, more relevant, concentrations is more unlikely. Bochmann has carried out extensive research into a series of more complex fluorinated anions based around BF_{15} which are of the form: $[\text{X}(\text{BAR}_3)_2]^-$ [$\text{X} = \text{CN}, \text{NH}_2, \text{N}(\text{CN})_2$; $\text{Ar} = \text{C}_6\text{F}_5, 2\text{-C}_6\text{F}_4(\text{C}_6\text{F}_5)$]. The idea was to create very weakly coordinating anions by delocalising the negative charge over multiple atoms. Accordingly in the case of $[\text{CN}(\text{BF}_{15})_2]^-$, the contribution of the anion to the activation energy of propene polymerisation with zirconocene catalysts was actually 1.1 kJ mol^{-1} less than $[\text{BF}_{20}]^-$. These anions can have an effect on both the activity and stereoselectivity during polymerisations [8, 139–143].

The solvents generally used in this chemistry are polar due to the ionic nature of the compounds and have been shown to form adducts with Group 4 cations in order to stabilise the active species. One such example that has been crystallographically characterised is $[\text{Cp}_2\text{ZrBn}(\text{C}_6\text{H}_5\text{Cl})][\text{BF}_{20}]$ (**25**) [144]. Other examples of halocarbon solvents bound to transition metals are known [144–147]. It is possible that the solvent-stabilised cations are resting states in the catalytic cycle and that the solvent needs to be removed from the metal centre before binding and subsequent polymerisation of the olefin can occur [4, 126, 148]. The cations in $[\text{Cp}^*\text{ZrMe}_2][\text{-MeBF}_{15}]$ and $[\{\text{Me}_2\text{Si}(\text{tBuN})(\text{C}_5\text{Me}_4)\}\text{ZrMe}][\text{BF}_{20}]$ are even stabilised by a molecule of hydrocarbon solvent (toluene) in solution and the former also in the solid state [133–135].



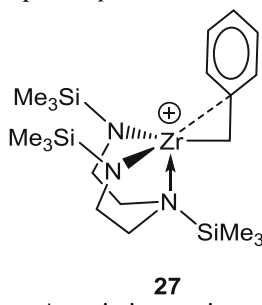
Non-classical interactions

Agostic interactions have been shown to be important in stabilising highly electrophilic cations [149, 150]. These interactions have also been proposed to play a key role in the polymerisation process. The $\mu\text{-Me}$ dication $[\text{Cp}^*_2\text{Ti}_2\{\text{-NC}(\text{N}^i\text{Pr}_2)\text{Ar}^{\text{F}_2}\}_2\text{Me}_2][\text{BF}_{20}]_2$ (**26**- $[\text{BF}_{20}]_2$, Fig. 9) has been characterised by X-ray crystallography and displays two agostic interactions for each methyl group, respectively [151]. $[\text{Cp}_2\text{TiMe}][\text{MeBF}_{15}]$ also exhibits α -agostic interactions which were not crystallographically characterised but determined using IR spectroscopy; neutral compounds such

as CpTiMe_3 and CpTiMeCl_2 have also been shown to display α -agostic interactions using the same method [150].

Computational studies by Clot and Eisenstein [152] have predicted that the α -agostic interaction is not so much a result of electron donation from the C–H σ -bond into the electron deficient metal centre, although this does occur, but is in fact better viewed as a second order Jahn–Teller distortion. Agostic interactions are identified by a short $\text{M}\cdots\text{HC}$ distance; these occur not primarily because the C–H bond is acting as a base, but because the tilt of the CH_3 group allows the σ_{CH_3} orbital to pick up an additional stabilising interaction from a different lower energy d -orbital. The extent to which this tilting occurs is a balance of the overlap and energetics involved. This is illustrated in Fig. 10. Tilting of the CH_3 group also allows a more efficient $\sigma(\text{C-H})$ interaction to occur with the metal centre.

Jordan et al. [153] have reported the β -C–H agostically stabilised species $[\text{Cp}'_2\text{Zr}(\text{PMe}_3)_2\text{C}_2\text{H}_5]^+$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) which contains a structurally characterised β -C–H agostic interaction. Green et al. [148] have used pendant phenyl groups to study agostic interactions in Group 4 alkyl cations. Another somewhat more prominent example of a non-classical interaction is that of the so called *ipso*-interaction which involves the η^2 -coordination of a benzyl group. An example of such an interaction was reported by Horton et al. [111] in an alkylzirconium complex supported by a tridentate diamide ligand (**27**). The $\text{Ti}\cdots\text{C}_{ipso}$ interaction manifests itself in the ^{13}C NMR spectrum showing a large $^1J_{\text{CH}}$ for the ZrCH_2 group (142 Hz) and an unusually upfield *ipso* carbon chemical shift (137.5 ppm).



Agostic interactions are also possible between Si and Me bonds and the metal centre. Compound **16** synthesised by Eisch et al. [104] displays a β -Si–C agostic interaction with the metal centre which is reflected in the upfield ^{29}Si NMR resonance ($\delta = -54.9$ ppm). Bochmann and Macchioni [154] also suggested their systems contained Si–Me agostic interactions which manifested itself as restricted rotation in the NMR spectra of compound $[\{\text{rac-Me}_2\text{Si}(\text{1-Ind})_2\}\text{-M}\{\text{CH}_2\text{SiMe}_3\}]^+$ ($\text{M} = \text{Zr}$ or Hf). Likewise Marks et al. [128] also suspected the presence of an agostic interaction in the complex $[(\text{C}_5\text{H}_3\text{Me}_2)_2\text{Zr}\{\text{CH}_2(\text{SiMe}_3)\}]^+$ which became evident in the low-temperature NMR spectra. Work by Mountford et al. [44, 155] in 2005 showed that treatment of $\text{Ti}(\text{N}^i\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\text{CH}_2\text{SiMe}_3)_2$ ($\text{Me}_3[9]\text{aneN}_3 =$

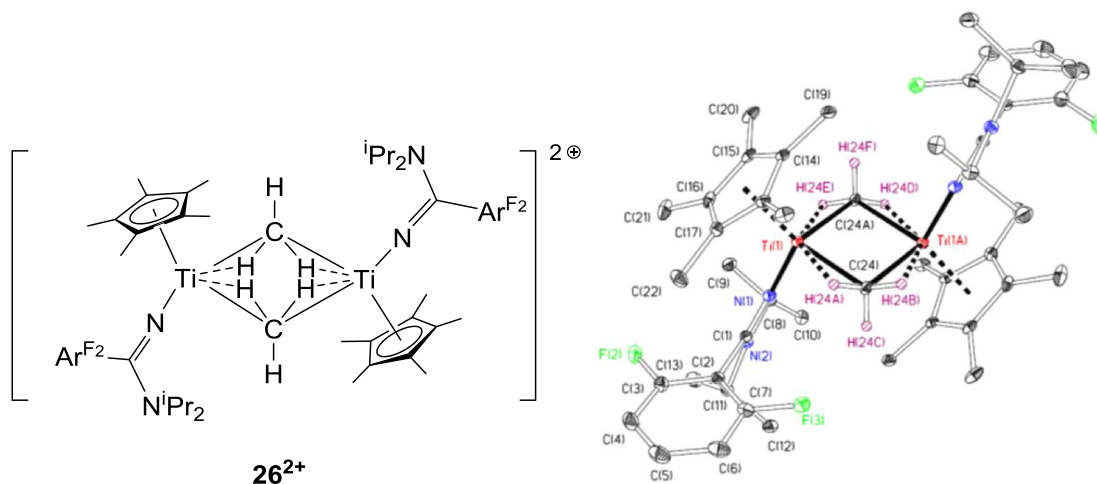


Fig. 9 Structurally characterised compound containing α -agostic interactions [151]

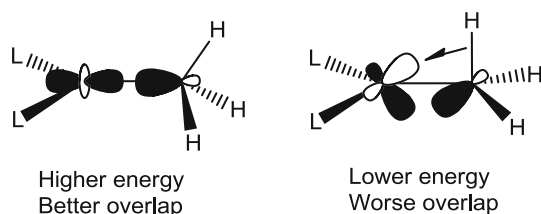


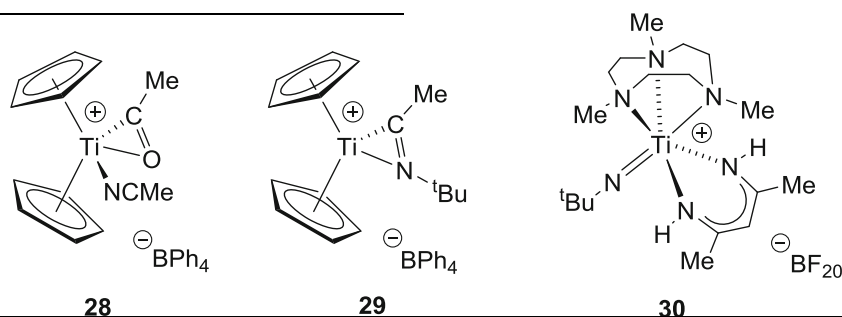
Fig. 10 Frontier orbitals involved in the formation of an α -agostic interaction

1,4,7-trimethyltriazacyclo-nonane) with TBF_{20} ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$) gave the species $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(-\text{CH}_2\text{SiMe}_3)][\text{BF}_{20}]$ in which the metal centre is stabilised by a β -Si-C agostic interaction as characterised by a high field ^{29}Si NMR resonance (-17.5 ppm).

point of view but can also help reveal mechanistic aspects of the polymerisation process [156].

Insertion chemistry of alkyl cations

The study of the insertion of unsaturated substrates into the metal alkyl bond is applicable to the understanding of the chain growth processes present in Ziegler–Natta polymerisation. As mentioned previously, in 1985 Eisch et al. showed that insertion of Me_3SiCCPh into the Ti–Me bond resulted in the formation of alkenyl complex **16**. Shortly after this discovery Bochmann et al. [106, 107] showed that base-stabilised cation $[\text{Cp}_2\text{TiMe}(\text{NCMe})]^+$ would react with CO to yield complex **28** and with $^t\text{BuNC}$ to yield complex **29**.



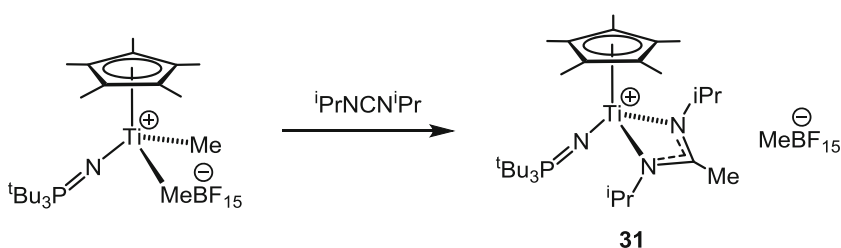
Reactions of alkyl cations

So far this tutorial review has centred on the formation and solution behaviour of Group 4 alkyl cations. This section gives a brief introduction into the types of reactivity that have been observed with these species. Reactivity of base-free cations is not only interesting from a fundamental

Treatment of $[\text{Cp}_2\text{TiMe}(\text{NCMe})]^+$ with nitriles PhCN and $^t\text{BuCN}$ produced a Lewis base adduct. However, with indenyl-supporting ligands and in the presence of excess nitrile, both PhCN and $^t\text{BuCN}$ undergo insertion into the Ti–Me bond within 1 h; this increase in reactivity is explained by the increased donor ability of indenyl vs. Cp. Insertion of MeCN and PhCN into the Ti–Me bond of

$[\text{Cp}_2\text{TiMe}][\text{BPh}_4]$ can occur but a longer reaction time is observed. For example, acetonitrile takes 2 weeks to react with the cation [106, 107, 157]. In 2006, Mountford et al. [44] showed that imido complex $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\text{NCMe}_2)(\text{NCMe})]^+$, produced initially from the insertion of acetonitrile into the Ti–Me bond of $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$, would rearrange to form a β -diketiminato complex (**30**) over 1 month. Insertion chemistry equivalent to that described above was exhibited by the analogous base-stabilised zirconocene cation **17**⁺ by Jordan et al. [98, 113, 158]. This reactivity is illustrated in Scheme 4.

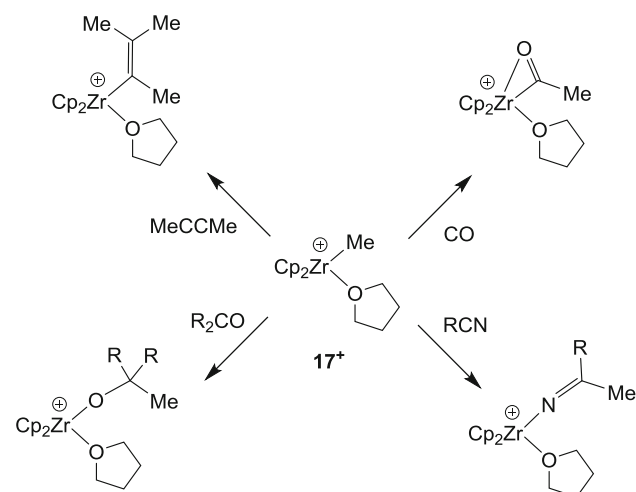
ethylene than nitriles and thus facile polymerisation of the ethylene. These nitrile reactions, therefore, help show that it is important to have an unstable metal–alkene intermediate in order for polymerisation of unsaturated species to occur. Post-metallocene species have also had their insertion chemistry studied. Stephan et al. [68, 160] have shown their ubiquitous phosphinimide-supported titanium and zirconium complexes will undergo insertion chemistry with carbodiimides and alkynes to give κ^2 -amidinate and alkenyl complexes, respectively; an example of a carbodiimide insertion to form **31** is shown in Eq. 4.



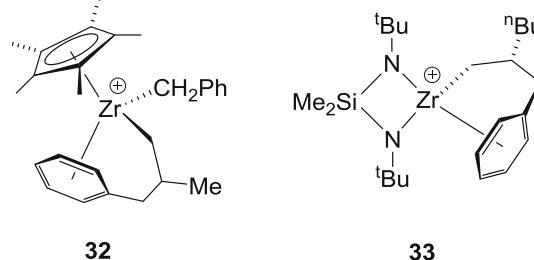
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Donor ligands (e.g. ethylene or nitrile) bond to $[\text{Cp}_2\text{TiMe}]^+$ by interacting with the metal's d_σ orbital [159]. In the case of nitriles, this complex is stable and isolable, whereas with ethylene, this is not the case (with electron-poor metals). The metal–nitrile complexes consequently experience a more significant activation barrier to migratory insertion than the unstable metal–ethylene complex. This crucially results in a much faster insertion into the metal alkyl bond for

The insertion of alkenes into M–C bonds of Group 4 cations has also been investigated. In 1994, Pellacchia et al. reported the synthesis of $[\text{Zr}(\text{Bn})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})][\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ by the insertion of propene into the Zr–C bond of $[\text{ZrBn}_3\{\eta^6\text{-PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}]$. Compound **32** was also synthesised by the insertion of propene into the Zr–C bond of $[\text{Cp}^*\text{ZrBn}_2]^+$ and was isolated and characterised by NMR spectroscopy and shown to contain a back-biting Ph–Zr interaction which acts to stabilise the cationic metal centre; this compound was later characterised by X-ray crystallography. The Ph–Zr interaction results in a stability in the complex towards both β -hydrogen elimination and further propene insertion. Other higher olefin insertion products could also be isolated and characterised [161].



Scheme 4 Reactions of **17**⁺ with unsaturated substrates. $[\text{BPh}_4]^-$ omitted



Horton et al. reported the products of alkene insertion into the Zr–CH₂Ph bond of diamide-supported complex $[\{\text{Me}_2\text{Si}(\text{NCMe}_3)_2\}\text{ZrBn}][\text{BF}_2\text{O}]$. Reaction with 1-hexene produced the isolable product **33**; the insertions of ethylene

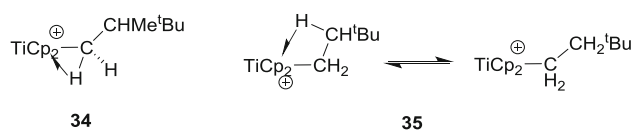


Fig. 11 Cations **34** and **35** stabilised by agostic interactions

and propylene could be observed on the NMR tube scale but the products could not be isolated. Compound **33** was also found to be stabilised by a Ph–Zr interaction as evident in the ^{13}C NMR. An interesting point to note is that the alkenes only reacted with the monomeric catalyst, and the dimeric catalyst persisted in solution [162]. Baird and Budzelaar [163–165] have also published papers in the past few years regarding the formation of titanium alkyl species resulting from alkene insertion into the Ti–Me bond.

Insertion of 3,3-dimethyl-1-butene (DMB) into the Ti–Me bond of the solvent-stabilised monomethyl cation $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)]^+$ results in the formation of complex **34** (Fig. 11), which can be characterised by NMR spectroscopy at 195–205 K. Compound **34** is stabilised by an α -agostic interaction which is reflected in the 7-ppm separation of the α -CH₂ protons and in the geminal coupling constant. Upon standing, **34** appears to undergo β -hydrogen elimination to give $[\text{Cp}_2\text{TiH}]^+$ which then inserts excess DMB to yield **35** which exists as a β -agostic-stabilised species in fast exchange with its non-agostic analogue [165]. A similar β -agostic-stabilised species is also formed from the reaction of $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)]^+$ with 2,4-dimethyl-1-pentene (DMP). In this reaction, Cp_2TiMe_2 is treated with $[\text{Ph}_3\text{C}][\text{BF}_{20}]$ (TBF_{20}) in the first step resulting in a mixture of species which are assigned as $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)][\text{BF}_{20}]$, $[\text{Cp}_2\text{TiMe}][\text{BF}_{20}]$ and $[(\text{Cp}_2\text{TiMe})_2(\mu\text{-Me})][\text{BF}_{20}]$. On addition of alkene, DMP only $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)][\text{BF}_{20}]$ reacted; $[\text{Cp}_2\text{TiMe}][\text{BF}_{20}]$ did not react with DMP or did it re-equilibrate to form $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)][\text{BF}_{20}]$. In the publication, it does note that a reviewer is not compelled by the existence of both $[\text{Cp}_2\text{TiMe}(\text{CD}_2\text{Cl}_2)][\text{BF}_{20}]$ and $[\text{Cp}_2\text{TiMe}][\text{BF}_{20}]$ and suggested the existence of a dimeric species [164].

Lewis acid–base chemistry

Alkyl cations are well known to form adducts with Lewis bases as previously mentioned, and the early examples of alkyl cations were isolated as adducts as previously discussed. Examples of Lewis bases used in this chemistry include RCN, PR_3 , THF, pyridine, NR_3 . Stronger donors such as PR_3 will replace moderately labile donors such as MeCN, but THF, being a weaker donor, will not [106]. The number of Lewis base donors that can bond to the metal centre is dependent on the radius of the metal. For example, titanium can form 16 valence electron complexes with a

single Lewis base, whereas zirconium can fit another ligand if small donor ligands are used and thus form 18 valence electron cations, e.g. $[\text{Cp}_2\text{ZrMe}(\text{PMe}_3)_2]^+$ [98, 166].

Bimetallic olefin polymerisation catalysts

Since the early 1990s, multimetallic catalysts have been explored in olefin polymerisation. Inspired by the role proximate metal centres play in increasing localised reagent concentration within enzymes, multimetallic species have been introduced to enhance several chemical transformations such as the Diels–Alder [167] and Stecker [168] reactions [169, 170]. In olefin polymerisation, a wide range of bimetallic catalysts have been employed to try and find any cooperative effect that would arise from the complimentary interaction of the polymeric chain between the adjacent metal centres. It took until the turn of the century for any beneficial properties to be observed, most notably, a higher molecular weight and superior chain branching. A particularly successful and readily studied family of bimetallic catalysts are the covalently tethered constrained geometry catalysts: for instance, the *ansa*-amido-monocyclopentadienyl Ti and Zr catalysts introduced by Li and Marks [171–173] (Fig. 12). This area has been comprehensively reviewed recently, and the reader is referred to this article for further details [169].

A study showed that **36** (Fig. 12) increases product polymer molecular weight by 130 times compared to its mononuclear analogue **37**, and that there are 13 and three times more ethyl branches per polymer chain than their mononuclear analogue for catalysts **36** and **38**, respectively. A stabilising agostic interaction between the propagating polymeric chain and the proximate metal centre results in a higher barrier to termination, thus generating a polymer with a higher molecular weight [171]. A computational study was carried out by Fragala and co-workers on catalyst **38** where *n*-octyl was used to represent a propagating chain and *n*-propyl was used to represent an oligomeric chain. The insertion and chain transfer transition states were analysed, and similar energetic values were seen for ethylene insertion in both cases. A consistent destabilisation (2 kcal mol^{-1}) was seen for the β -hydrogen chain transfer of catalyst **38** with an *n*-octyl chain, attributable to steric repulsions resulting from the constraints from the stabilising agostic interaction (Fig. 13). Molecular weight is proportional to the ratio of the rates of propagation to termination of the reaction, and therefore, the reduced termination corresponds to an increase in molecular weight [174].

The increase in branching is proposed to arise from the recapture of the vinylic end of the polymer at the neighbouring metal centre after chain transfer. This process aids an intramolecular re-insertion into the growing polymeric

Fig. 12 Covalently tethered Group 4 bimetallic constrained geometry catalysts (M = Ti or Zr) [170]

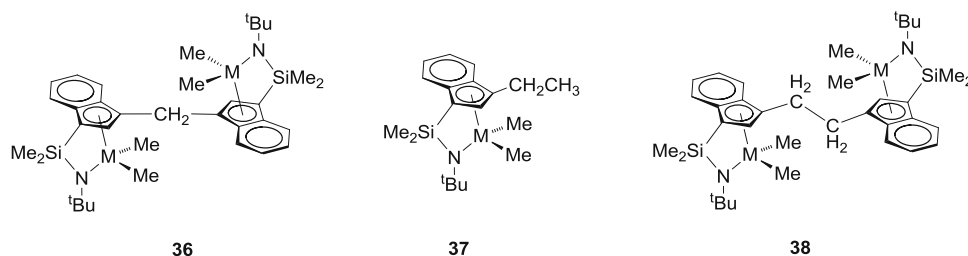
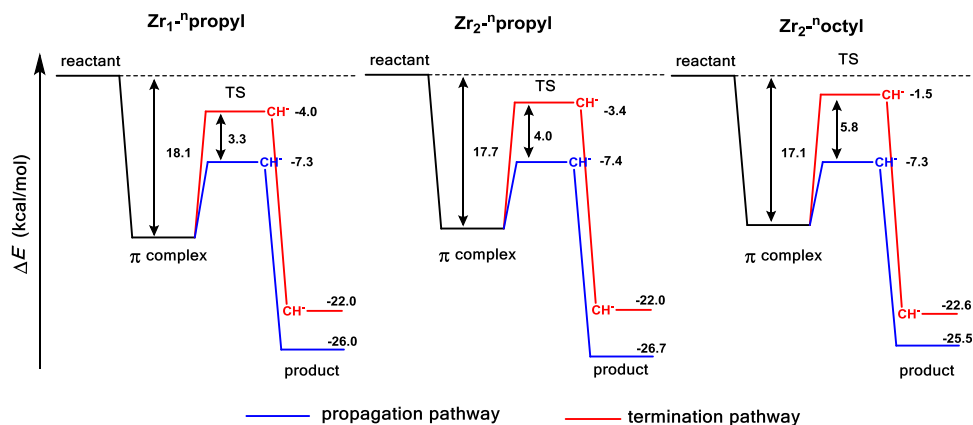


Fig. 13 Reaction pathway describing the propagation and termination routes in ethylene homopolymerisation. Zr_1 and Zr_2 represent catalysts **37** and **38**, respectively [174]



chain. The computational study, introduced above, also refined the geometrical orientation of an oligomeric π -bonded vinyl terminated oligoethylene chain; a non-negligible (2 kcal mol^{-1}) stabilisation energy is observed with the second metal site, a pre-requisite for ethyl branching [174].

A secondary interaction is also seen when alternative monomers are activated. Ethylene/hexene and ethylene/styrene copolymerisations using the titanium analogue of **38** show a higher α -olefin incorporation. In the case of the styrene homopolymerisation, the binuclear catalysts show a significantly higher yield and activity than their mononuclear analogue. In the mononuclear counterpart, the styrene 2,1 insertion product results in the deactivation of the metal centre. However, when using the bimetallic species, 1,2 and 2,1 insertion compete equally. This suggests an unusual insertion regiochemistry, which the authors suggest is a result of a favourable interaction with the proximate metal centre as is depicted in Fig. 14 [175, 176].

Another explored capacity of the bimetallic catalysts is their use in copolymerisation of severely encumbered isoalkenes without ring opening or rearrangements. Methylene cyclopentane, methylenecyclohexane and 2-methyl-2-butene are all incorporated into the polyethylene backbone under mild conditions with catalysts **38** and **36**. The presence of bulky cycloalkane rings along the polymeric chain frustrates the tendency to coil, altering the physical properties of the product polymer [173].

Although so far only one family of Group 4 bimetallic catalysts have been described, a wide range of covalently tethered alternatives have been investigated with varying

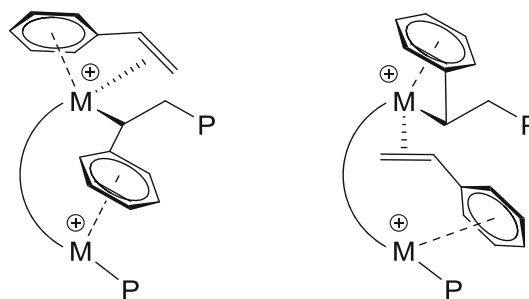
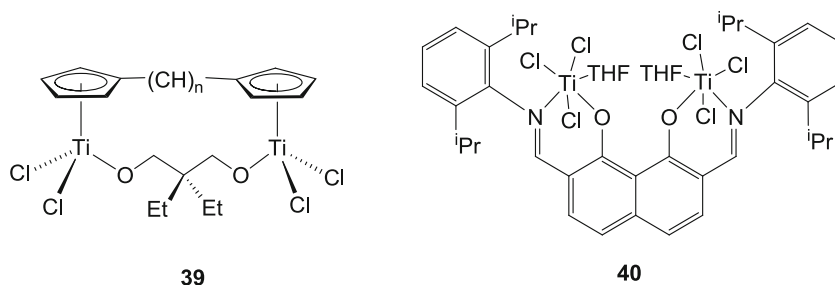


Fig. 14 Proposed competing regiochemistry forms in the homopolymerisation of styrene [175]

successes. Phenylene [177–179]-, polymethylene [180–182]-, and silyl [183, 184]-bridging moieties have all been shown to have some cooperative effects resulting in increased molecular weight or improved comonomer incorporation. Configurationally restrained ligands give an alternative to their flexible counterparts by maintaining proximate metal centres. This was effectively shown by Noh and co-workers [185] who introduced a doubly bridged ligand (**39**, Fig. 15), which produces a higher activity, molecular weight and tacticity in styrene polymerisation, and later by Marks [186] with the use of a naphoxydiiminato ligand (**40**, Fig. 15).

In 2002, Marks and co-workers demonstrated that using both a titanium and a zirconium mononuclear *ansa*-monocyclopentadienyl-amido catalyst in situ results in a bimodal GPC (gel permeation chromatography) plot, which corresponds to the two separate active sites. When the bis(borate) cocatalyst $[\text{CPh}_3]_2[(\text{C}_6\text{F}_5)_3\text{B}(1,4\text{-C}_6\text{F}_4)\text{B}(\text{C}_6\text{F}_5)_3]$ is

Fig. 15 Examples of configurationally constrained Group 4 catalysts [185, 186]



employed, only a single site is seen, synonymous with the predominance of a single homogeneous catalytic species [187]. Other heterobimetallic species, using both early and late transition metals, have been synthesised in order to increase the efficiency of “tandem catalysis”, where the polymer properties produced by different metal centres are incorporated into the same polymer product [188–191].

Concluding remarks

This tutorial review has provided an introduction to homogenous Group 4 olefin polymerisation catalysts, starting from the early days of metallocene chemistry, to the so-called post-metallocene systems. It has shown how electron-deficient cations can be generated and trapped, and highlighted a number of key roles of these complexes in catalytic systems. Finally, an introduction to bimetallic catalysts was provided, which suggests one of the way forward strategies to be adopted in the future for developing new catalysts with improved performance.

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