Cationic Group 4 metallocene complexes and their role in polymerisation catalysis: the chemistry of well defined Ziegler catalysts*

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Cationic alkyl complexes of Group 4 metallocenes of the type $[MCp_2R]^+$ (M = Ti, Zr or Hf, Cp = C_5H_5) have been recognised as the catalytically active species in metallocene-based olefin polymerisation catalysts. These highly electrophilic 14-electron species possess a very complex chemistry in which the formation of temporarily dormant stabilised adducts plays a dominant role. Cationic metal alkyls of this kind are found to be extremely active polymerisation catalysts, with high stereoselectivities and the potential to produce numerous previously inaccessible polymeric materials. A detailed understanding of the chemistry of these species promises to lead to a new generation of well defined polymerisation catalysts. Metallocene-based catalysts already play an increasing role in major industrial polymerisation processes.

Since Ziegler's discovery of the polymerisation of ethylene with $TiCl_4$–$AlClEt_2$ catalysts just over 40 years ago,[1] shortly followed by Natta's discovery of the stereoselective polymerisation of propene,[2] the polymerisation of α-olefins has developed into a giant industry. World production of polyolefins in 1995 is estimated to be 53.6 million tons, twice the figure of 1983, and is expected to grow by 50% over the next 10 years.[3] This industry is based on heterogeneous catalysts which, after four decades of development, have become highly selective and efficient. Classical Ziegler catalysts are heterogeneous, with the polymerisation taking place on dislocations and edges of $TiCl_3$ crystals (cf. structures **26a** and **26b** below). Consequently, there are many different types of active sites, and the resulting polymer has a typically broad molecular weight distribution.[4] Alternatives are chromium-based catalysts, e.g. Cr on silica (Phillips catalyst) which are comparatively less active and polymerise ethylene to give high-molecular-weight rigid polymethylene-type polymers; they are inactive towards propene. Heterogeneous titanium-based Ziegler catalysts, on the other hand, are more versatile; they are able to polymerise propene with a very high degree of stereoselectivity and catalyse the copolymerisation of ethylene with higher alk-1-enes such as hex-1-ene, important for the production of flexible, non-brittle polymers for use as films and in packaging. Although these are successful processes which give rise to a wide range of polymer products, the diversity of active sites in heterogeneous catalysts leads to an uneven degree of comonomer incorporation, with a high incorporation rate in short chains, and little incorporation in the high-molecular-weight fraction, a drawback where metallocenes offer particular promise.

By the 1980s it appeared that the development of heterogeneous catalysts was maturing rapidly, with few major advances expected. At this juncture several developments in the chemistry of metallocenes came together to produce a further quantum leap in polymerisation catalysis.

Shortly after the synthesis of the first Group 4 metallocenes by Wilkinson et al.[5] in 1953 the use of these complexes as polymerisation catalysts was tested. Mixtures of $[TiCl_2Cp_2]$ and $AlClEt_2$ were found to polymerise ethylene with comparatively moderate activity; propene was not polymerised.[6,7] These catalysts were however prone to reduction to inactive titanium(III) species and could not compete with the highly active and stereoselective heterogeneous catalysts.

Consequently they found no industrial application, although these soluble systems were of value for mechanistic studies.

An important further development began with the unexpected observation that although Ziegler catalysts are very sensitive to hydrolysis, traces of water actually increased the rate of polymerisation in titanocene catalysts, and the formation of aluminoxanes by partial hydrolysis of the aluminium alkyl components was suggested.[8,9] This phenomenon was investigated in detail by Sinn and co-workers who found that the normally inactive system $[ZrCp_2Me_2]$–$AlMe_3$ becomes highly active upon the addition of water.[10] The same effect is achieved when $AlMe_3$ is partially hydrolysed to methylaluminoxane (MAO) before the transition-metal complex is added. Methylaluminoxane is a poorly characterised polymeric glassy substance, usually of molecular weight 900–1200 and the approximate composition $[\{MeAlO\}_n]$, which consists of linear, cyclic and cross-linked compounds, probably containing predominantly four-co-ordinate Al centres and some $OAlMe_2$ end groups.[11] The compound dissolves readily in hydrocarbons such as toluene where, due to the facile ligand exchange in aluminium complexes, it establishes complex solution equilibria. Samples are usually rich in methyl groups, and even after drying *in vacuo* contain typically 3–4% free Al_2Me_6;[12] in commercial MAO samples as much as 30–40% trimethylaluminium may be present. Repeated pumping leads to loss of Al_2Me_6 and the increasing formation of an Al_xO_y network which no longer dissolves in toluene. The Al_2Me_6 content in MAO solutions guards against such heterogenisation. As Sinn and co-workers[10] found, MAO is a much more effective activator for metallocene dihalides than aluminium alkyl halides and even allows the polymerisation of propene with $[ZrCl_2Cp_2]$ (although these simple Cp complexes lack the stereoselectivity of the heterogeneous catalysts). In order to achieve high activity, MAO has to be employed in a large excess over the zirconocene component, usually at Al:Zr ratios of 10^3–10^4:1, so that in such catalysts the cost of MAO by far outstrips that of the zirconium complex. In spite of this drawback MAO has become the most widely used activator for metallocene-based catalyst systems, including large-scale industrial processes.

Mechanistic Aspects

Although metallocene-based catalysts are, as soluble systems, in principle more amenable to mechanistic study than heterogeneous catalysts, it proved for a long time rather

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* *Non-SI units employed:* cal = 4.184 J; bar = 10^5 Pa.

difficult to underpin the various mechanistic ideas with firm experimental evidence. In 1959 Breslow and Newburg[13] suggested for their [TiCl$_2$Cp$_2$]–AlClEt$_2$ system that the transition metal is first alkylated and then forms a halide-bridged binuclear complex which is capable of reaction with ethylene (Scheme 1). Some polarisation of the molecule was envisaged with a partial positive charge on titanium and negative charge on aluminium.[13] This proposal anticipated several features of the well known Cossee–Arlman polymerisation mechanism[14] for heterogeneous catalysts, such as the Lewis acidity of the metal centre and the mutual *cis* orientation of the metal–alkyl bond and the incoming monomer ligand. There was subsequently some debate about the nature of the active species and it was widely assumed that a probably halide-bridged titanium–aluminium mixed-metal species was involved. Various plausible intermediates were suggested, for example as formulated by Henrici-Olivé and Olivé (Scheme 2).[15]
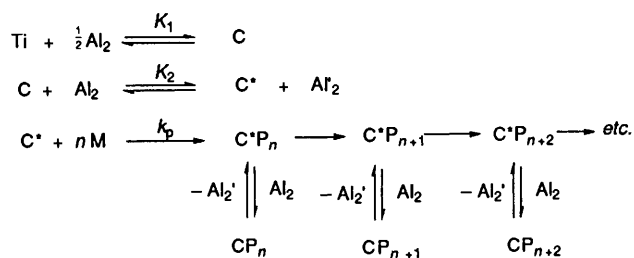
Kinetic studies on [TiCl$_2$Cp$_2$]–AlClR$_2$ polymerisation systems provided indications of an 'intermittent' chain-growth mechanism.[16] A mechanistic scheme was proposed in which the well known adduct between the titanocene complex and the aluminium alkyl is converted into an active species C* which is able to insert ethylene molecules. After each insertion step the active complex carrying a polymer chain, C*–P, can become temporarily dormant as a stabilised complex which is
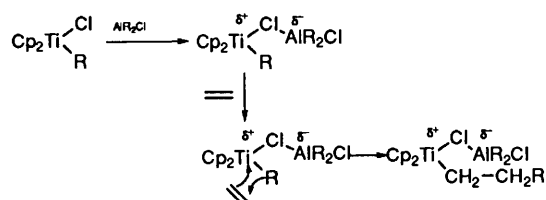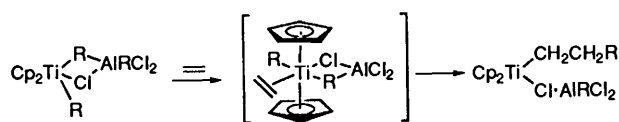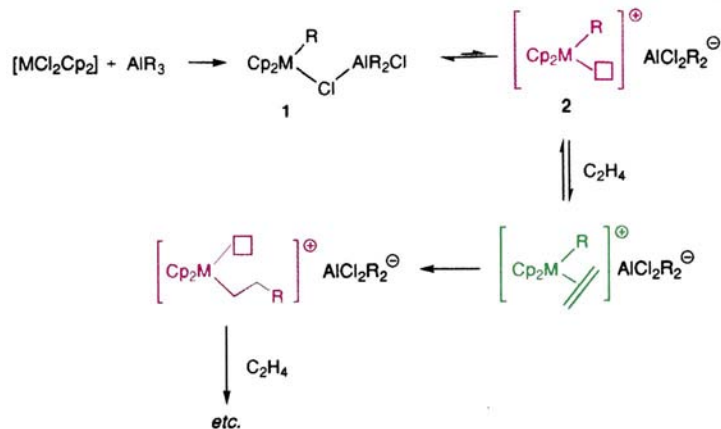
spectroscopically detectable. Renewed activation then allows further chain growth (Scheme 3). These studies did not, of course, provide information about the nature of C*; they did however indicate that any metal–olefin π complex involved could only be present in minute concentrations. The studies also provided an estimate of the relative rates of ethylene insertion into Ti–R bonds; Ti–Me reacts with C$_2$H$_4$ 120 times slower than Ti–Et and 96 times slower than Ti–Pr, in line with the observation that in this and other systems rapid chain growth is already observed when substantial amounts of potentially reactive Ti–Me species are still present in the system.[16]
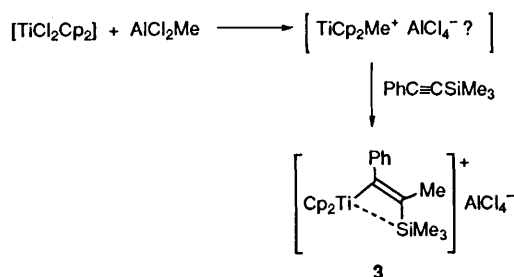
The chain growth sequence outlined in Scheme 3 is compatible with the assumption of electron deficient cationic intermediates, [Cp$_2$Ti–R]$^+$ (2), as the active species C* (Scheme 4). Such a cationic 14-electron complex could be formed by dissociation of the adduct 1 and would possess a co-ordination site suitable for binding an olefin molecule *cis* to the Ti–alkyl bond, ready for facile alkyl migration and chain growth (alkene 'insertion'). After each step the anion, here [AlCl$_2$R$_2$]$^-$, would be able to occupy this co-ordination site with formation of a halide-bridged bimetallic complex, representing the temporarily dormant spectroscopically observable species C–P$_n$ of Scheme 3.

The possibility of the participation of a cationic active species [TiCp$_2$Me]$^+$ had been suggested by Shilov and co-workers as early as 1961.[17] There was, however, no direct evidence for the existence of such a species. Dyachkovskii attempted the electrochemical generation of [TiCp$_2$Me]$^+$ in dichloromethane and indeed found that ethylene polymerisation took place only in the cathode chamber.[18] However, the idea of ionic intermediates did not find widespread acceptance as an explanation for a reaction which typically took place in very non-polar solvents. Interest was revived by the discovery of Eisch *et al.* in 1985 that Ph–C≡C–SiMe$_3$ reacted with [TiCl$_2$Cp$_2$] in the presence of AlCl$_2$Me to give the cationic titanium vinyl complex 3 (Scheme 5) formally the product of alkyne insertion into a postulated '[TiCp$_2$Me]$^+$' intermediate.[19]

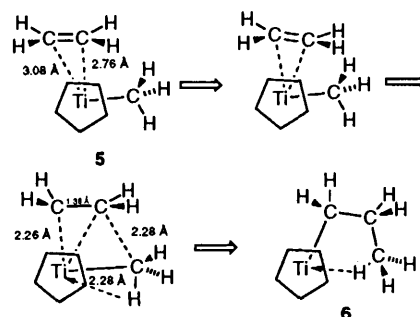In the following year we reported the synthesis of the first cationic titanocene methyl complexes, [TiCp$_2$Me(L)]$^+$X$^-$ (L = NH$_3$, NCR, pyridine, *etc.*; X = PF$_6$ or BPh$_4$).[20] Although the presence of strongly bound donor ligands L prevented any reactions with ethylene, the complexes readily underwent insertion reactions with nitriles.[20,21] At around the same time Jordan *et al.* reported analogous cationic zirconium complexes [ZrCp$_2$Me(L)]BPh$_4$, including the labile tetrahydrofuran (thf) complex which partially dissociates in dichloromethane and polymerises ethylene; the first evidence that well defined cationic metallocene complexes were capable of polymerising olefins in the absence of aluminium alkyl activators.[22] The related benzyl complex [ZrCp$_2$(CH$_2$Ph)(thf)]BPh$_4$ was similarly active for the polymerisation of ethylene but not propene,[23,24] as were the titanocene–ether complexes [TiCp$_2$Me(L)]BPh$_4$ (L = thf, Et$_2$O or PhOMe).[25]

Scheme 1

Scheme 2

$$\text{Ti} + \tfrac{1}{2}\text{Al}_2 \underset{}{\overset{K_1}{\rightleftharpoons}} \text{C}$$

$$\text{C} + \text{Al}_2 \underset{}{\overset{K_2}{\rightleftharpoons}} \text{C}^\bullet + \text{Al'}_2$$

$$\text{C}^\bullet + n\text{M} \xrightarrow{k_p} \text{C}^\bullet\text{P}_n \longrightarrow \text{C}^\bullet\text{P}_{n+1} \longrightarrow \text{C}^\bullet\text{P}_{n+2} \longrightarrow etc.$$

CP$_n$ CP$_{n+1}$ CP$_{n+2}$

Scheme 3   C* = active [TiCl$_2$Cp$_2$]–AlClR$_2$ polymerisation species, P = polymer chain

Scheme 4

Scheme 5

Scheme 6

4a   **4b**
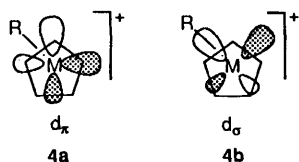
Although the activities of these donor-stabilised cationic complexes were at best modest, they did play a useful role as models for the active species. The details of the interaction of ethylene with $[MCp_2Me]^+$ has been the subject of numerous theoretical studies at various levels of sophistication. The results tend to be quite sensitive to the methods used and differ in the importance attached to features such as the presence or absence of agostic interactions, the relative stability of the ethylene π-complex and the height of the activation barriers. However, all agree on the general features such as the necessity of generating a 14-electron $[MCp_2R]^+$ species. Such a complex has two low-lying unoccupied orbitals, d_π (**4a**) and d_σ (**4b**).[26] The d_σ orbital acts as the acceptor for the incoming ethylene molecule. The trajectory of the approach of the co-ordinated olefin towards the alkyl chain on the way to forming the new C–C bond is shown in Scheme 6, based on the *ab initio* calculations by Jolly and Marynick.[27] The interatomic distances for the optimised transition-state geometry shown in Scheme 6 correspond quite closely to the results obtained by Ziegler and co-workers for the analogous zirconium reaction $[ZrCp_2Me]^+ + C_2H_4$ using density function methods.[28]

The details of the chain growth mechanism and the structure of the transition state have attracted considerable attention, not least because of the implication for the stereocontrol in the polymerisation of alk-1-enes. In 1983 Brookhart *et al.* suggested that the insertion step may be facilitated by an α-agostic interaction of one C–H bond of the alkyl ligand with the Lewis-acidic metal centre.[29] This is only possible if the alkyl ligand adopts the conformation shown for the CH_3 ligand in **5** (Scheme 6), rather than the conformation resulting from a rotation by 60°. Jolly and Marynick suggested for $[TiCp_2Me(C_2H_4)]^+$ that structure **5** may be primarily adopted in order to avoid unfavourable interactions between CH_3 and the Cp ligands, rather than because of a strong energy gain by a Ti$\cdots$HC interaction.[27] By contrast, recent *ab initio* calculations by Ahlrichs and co-workers suggest strong α-agostic bonding of one methyl hydrogen in $[TiCp_2Me]^+$, to the point of an almost 'carbenoid' character of the methyl ligand. These authors do not find any significant role for an ethylene pre-complex on the potential energy surface, suggesting that the insertion proceeds without definable intermediates or indeed without a noticeable activation barrier.[30] Others[27,31] have calculated activation barriers of 7–10 kcal mol⁻¹, in good agreement with experimentally determined values,[32] and find comparatively high ethylene binding energies of 20–30 kcal mol⁻¹ which increase in the order Ti < Hf ≤ Zr.[31]

There is evidence from both Extended Hückel[33] and *ab initio* calculations[34] that the alkene complex $[ZrCp_2Me(C_2H_4)]^+$ does not initially possess α-agostic interactions but that these

develop as the CH_3 ligand tilts away from the Zr–C axis towards the C_2H_4 ligand, with CH_3 and C_2H_4 hydrogens in eclipsed conformations. This interaction stabilises the transition state, with a very low activation barrier (if any). The whole insertion sequence is quite exothermic, $\Delta G < -30$ kcal mol⁻¹.[31]

The participation of an α-agostic interaction during the chain growth process has been elegantly demonstrated by Brintzinger and co-workers[35,36] for the hydrodimerisation of *E*- and *Z*-BuCH=CHD (Scheme 7). Since Zr$\cdots$HC is favoured over Zr$\cdots$DC the presence of agostic bonding in the rate-determining step would lead to an unequal distribution of *erythro* and *threo* products from a non-chiral catalyst, and indeed a stereokinetic isotope effect of 1.3:1 (*erythro–threo*) has been found.[35] Scandium catalysts show a similar isotope effect.[37]

The primary product of the insertion, the propyl complex **6** (Scheme 6), is also stabilised by an agostic interaction, this time with a γ-CH bond. It has been suggested that there is a subsequent rearrangement to a more stable β-agostic structure which may represent a 'resting stage' in the catalytic process[36] although there may be a substantial energy barrier for such a γ→β rearrangement.[31]

Surprising results concerning the speed of the insertion process were recently obtained with *ab initio* molecular dynamics simulations on $[H_2Si(C_5H_4)_2ZrMe]^+ + C_2H_4$.[34] The whole ethylene insertion process seems to take place on a 70–170 fs time-scale. During this process the $H_2Si(C_5H_4)_2$ ligand framework proved to be remarkably flexible, with (C_5H_4)–Si–(C_5H_4) angles changing from *ca.* 75 to 98 and back to 75°. No doubt these figures will be revised; they underline however the extraordinarily high catalytic activities one might expect from these catalysts in the absence of other mitigating influences.

A consequence of the insertion sequence of Scheme 6 is the alternation of the site for monomer co-ordination after each insertion step, a facet that becomes crucial for the stereocontrol of alk-1-ene polymerisations (Scheme 8).

Chain termination occurs typically *via* β-hydride elimination, a process that is about three orders of magnitude slower than the insertion step. For propene oligomerisations with sterically hindered $[Zr(C_5Me_5)_2R]^+$ catalysts termination by β-methyl transfer has also been observed.[38] Energetically, β-CH_3 elimination is preferred,[39] while β-H elimination is kinetically more facile. The resulting $[Cp_2M-H]^+$ fragment rapidly initiates the growth of a new polymer chain.

Synthesis and Chemistry of Electron-deficient $[Cp_2M-R]^+$ Cations

The mechanistic discussion in the previous section is based on the assumption that 14-electron species $[MCp_2R]^+$, however transient, are formed in catalytically active systems, independent of the nature of the 'activator' (*e.g.* $AlClEt_2$ or MAO). The concentration of $[MCp_2R]^+$ in such mixtures is of course not known, and conventional metallocene–aluminium alkyl mix-
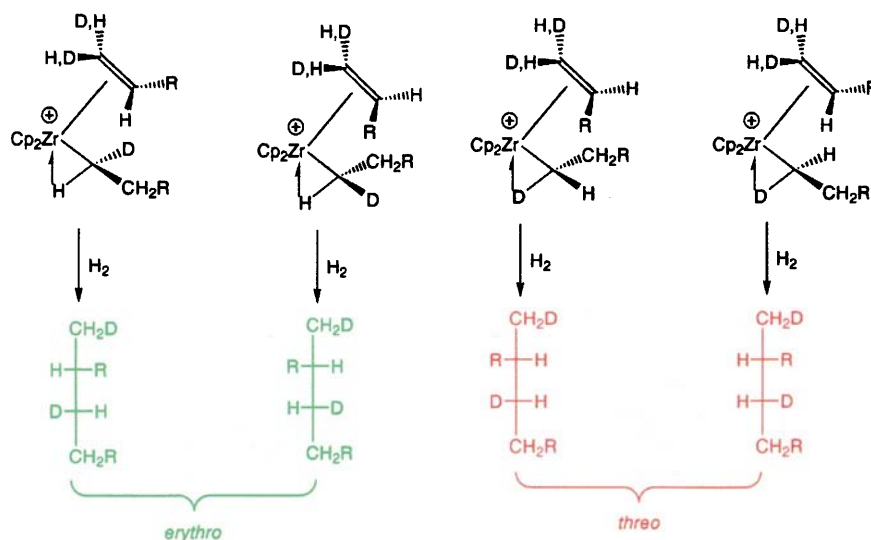
Scheme 7
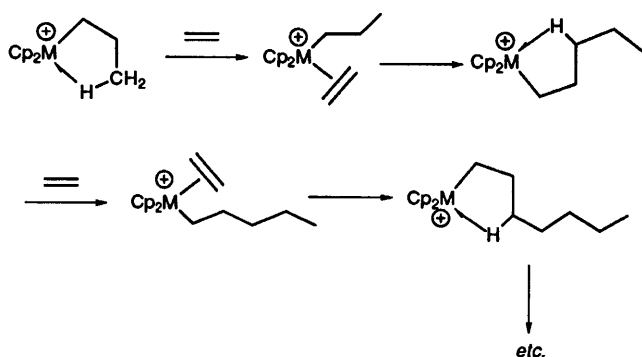
Scheme 8
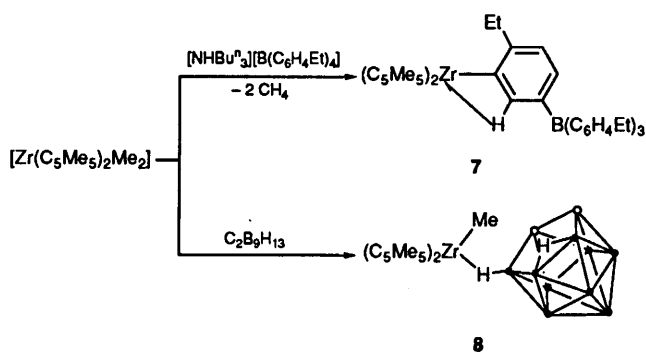
Scheme 9

tures are far too complex to identify reactive intermediates or to determine their lifetimes, resting and active stages, or decomposition pathways. A direct synthesis of 'base free' $[MCp_2R]^+X^-$ would not only confirm mechanistic assumptions and allow the underlying chemistry of such complexes to be studied, but might also lead to the preparation of essentially 'neat' catalytically active sites and therefore provide catalysts of extremely high activity.

Early studies had shown that even donor-stabilised metal alkyl cations are very potent electrophiles which do not tolerate conventional 'non-co-ordinating' anions such as BF_4^- and PF_6^- but form isolable salts with BPh_4^-.[20,21,22] These studies have also established the protolysis of metallocene dialkyls with ammonium salts as a general route to cationic metallocene derivatives [equation (1)].[20,25]

$$[MCp_2R_2] + [NHR'_3]X \longrightarrow$$
$$[MCp_2R]^+X^- + RH + NR'_3 \quad (1)$$
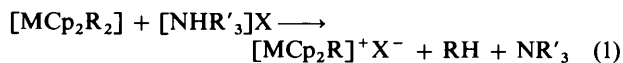
In 1989 Turner and co-workers[40] reported the formation of the zwitterionic complex **7** from the reaction of [Zr-Cp*$_2$Me$_2$] (Cp* = C$_5$Me$_5$) and [NHBu$_3$][B(C$_6$H$_4$Et-3)$_4$] in toluene. Similarly, the reaction between [ZrCp*$_2$Me$_2$] and the acidic *nido*-carborane C$_2$B$_9$H$_{13}$ gave **8** in which the anion is co-ordinated *via* a hydride bridge (Scheme 9). Both complexes polymerise ethylene rapidly under mild conditions.[40] Complex **7** evidently arose by electrophilic attack of [ZrCp*$_2$Me]$^+$ on the anion. The first cationic 'base free' titanium and zirconium complexes [MCp'$_2$Me][BPh$_4$] were obtained from [MCp'$_2$Me$_2$] and [NHMe$_2$Ph][BPh$_4$] in dichloromethane at $-40\,°C$ in essentially quantitative yield (M = Ti or Zr, Cp' = C$_5$H$_5$ or η^5-indenyl).[41] Under these conditions the compounds are presumably present as dichloromethane solvates. The injection of *ca.* 5 equivalents of ethylene to solutions of [TiCp'$_2$Me]$^+$ (Cp' = indenyl) resulted in the formation of polyethylene, while most of the Ti–Me complex remained unreacted, a behaviour reminiscent of the kinetic results by Fink and co-workers on [TiCl$_2$Cp$_2$]–AlClMe$_2$ systems.[16] Although [TiCp'$_2$Me]$^+$ proved to be thermally labile in chlorinated solvents, the complex polymerised not only ethylene but also propene, in contrast for example to the [TiCl$_2$Cp$_2$]–AlClEt$_2$ catalysts. An analogous reaction allowed the isolation of [TiCp*$_2$Me]BPh$_4$;[42] like similar pentamethyl-cyclopentadienyl titanium complexes [TiCp*Me(L)]$^+$ (L = thf or tetrahydrothiophene)[43,44] this compound is catalytically inactive, presumably for steric reasons.

These studies showed that although equation (1) indicates the formation of a single species, the *in situ* generation of cationic catalysts leads in fact to a complex equilibrium of various adducts of the highly electron-deficient [MCp'$_2$R]$^+$ cation. The amine liberated during the protolysis step, the counteranion and the solvent are capable of binding to [MCp'$_2$R]$^+$. Under polymerisation conditions this means that all these adducts are in competition with the only productive species, the olefin complex (Scheme 10). Although the notion of 'single site' catalysts for metallocenes[45,46] is an apt description as far as the transition state is concerned, it is evident that there is a whole range of resting states the concentration of which must be minimised in order to obtain highly productive catalysts. Only if the relative importance of these equilibrium complexes and the underlying chemistry are known can one begin to estimate the proportion of species that are productive at any one time, and hence evaluate actual catalyst activities.

The most important contribution in these equilibria is the co-ordination of the counteranion.[47] For the tetraphenylborate anion various types of interaction with electron-deficient metal centres have been found; examples are complexes **9–11**.[48–50]
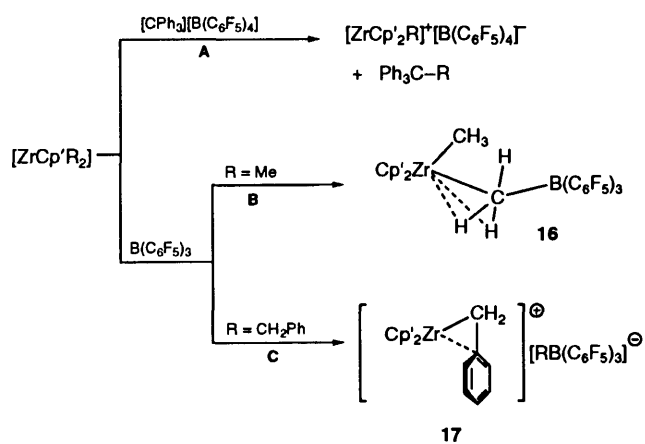
Scheme 10

9

10

11

12

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14

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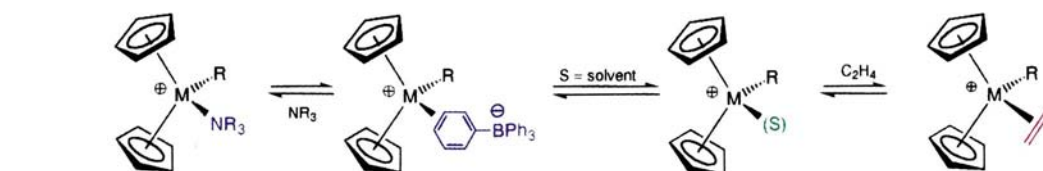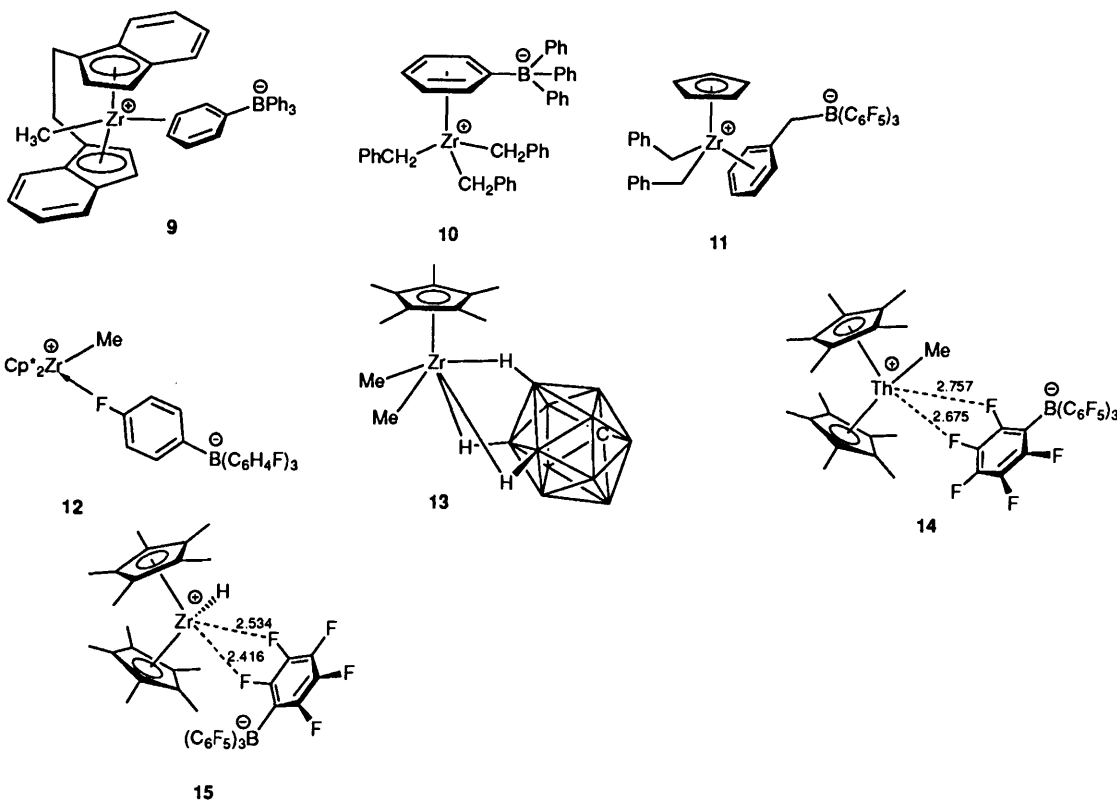
Fluoro-substituted tetraarylborates are less basic, although $[B(C_6H_4F-4)_4]^-$ has been shown to co-ordinate via a single F atom, as in **12**.[51]

The role of carboranes as comparatively non-co-ordinating anions has been mentioned above (Scheme 9).[40] There has been some success with $[ZrCp_2Me]^+$ salts of anions of the type $[M(C_2B_9H_{11})_2]^-$ (M = Fe, Co or Ni); these catalysts possess considerable activity for the polymerisation of ethylene and for ethylene–butene copolymerisation.[52] On the other hand, carboranyl anions can act as polydentate ligands as in **13** to give species of very low catalytic activity.[53c]

A substantial reduction in cation–anion interaction was achieved with Turner's introduction of perfluorotetraphenyl-borate $[B(C_6F_5)_4]^-$ as the counteranion.[54] This borate is considerably less basic and less prone to phenyl transfer reactions than $[BPh_4]^-$ and has produced cationic polymeris-ation catalysts of exceptionally high activity.

Cationic complexes can be generated from Group 4 metal alkyls either by protolysis using salts of very weakly basic amines such as $[NHMe_2Ph][B(C_6F_5)_4]$ or, if amine as the by-product is to be avoided, by alkyl-anion transfer with $[CPh_3][B(C_6F_5)_4]$ (Scheme 11, pathway A).[55,56] However, although $[B(C_6F_5)_4]^-$ comes close to the ideal of a 'non-co-ordinating anion', at least in dilute solutions, even here there are detectable metal–fluoride interactions in many cases. For example, the crystal structure of the thorium complex $[ThCp^*_2Me][B(C_6F_5)_4]$ (**14**) shows close Th $\cdots$ F contacts of 2.675 and 2.757 Å. The ethylene polymerisation activity of **14** is about 3500 times higher than that of the $[BPh_4]^-$ analogue.[57] In the zirconium hydride complex **15** a similar weak co-ordination to two F atoms of $[HB(C_6F_5)_3]^-$ was found, which

Scheme 11

was surprisingly favoured over anion co-ordination via the B–H moiety.[58]

As an alternative to the synthesis of cationic complexes Marks and co-workers introduced the reaction of metallocene dimethyls with $B(C_6F_5)_3$ to give methyl-bridged zwitterionic complexes of type **16** (Scheme 11, pathway B).[59] This route offers the advantage that the product is stabilised by methyl co-ordination and is less polar and significantly more soluble in toluene. Several such complexes have been characterised by X-ray diffraction.[59,60] The $Zr–CH_3–B$ bridge is compar-atively weak, with rather long Zr–C distances which depend on the steric requirements of the Cp ligands. Two of the

Scheme 12

18a, Cp' = C5Me5
18b, Cp' = C5H3(SiMe3)2

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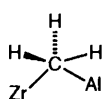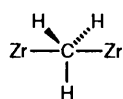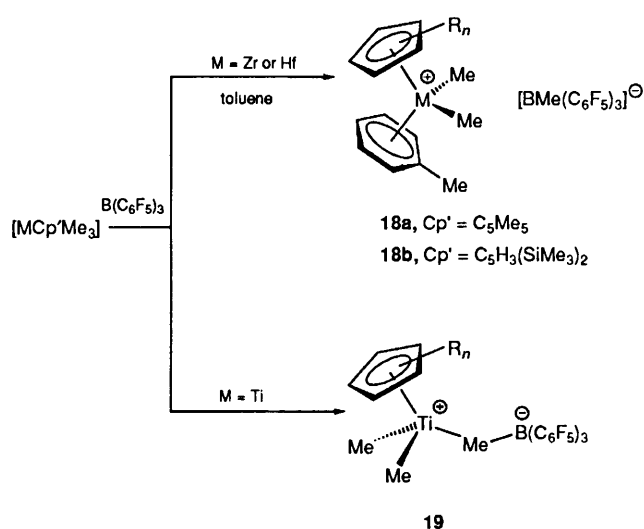
methyl hydrogens are agostically bonded to zirconium. It is thought that under catalytic conditions **16** partly dissociates to $[ZrCp'_2Me]^+[BMe(C_6F_5)_3]^-$, and indeed complexes of structure **16** are good ethylene polymerisation catalysts.

As is generally the case, the activity of **16** depends on the bulkiness of the Cp' ligands. If $Cp' = C_5H_5$ or $C_5H_3Me_2$-1,2, the activities are comparable to those of the analogous $[ZrCl_2Cp_2]$–MAO catalysts. Hydrogenolysis of **16** leads to the cationic hydrides $[ZrHCp'_2]^+$; these react with propene to give low-molecular-weight polymers (Cp' = C_5Me_5 or $C_5H_3Me_2$), while the bulkier $[ZrH(C_5H_3Bu^t_2$-1,3)_2]^+$ selectively dimerises propene to 2-methylpentenes.[59b]

In contrast to the methyl complexes the reaction of zirconocene dibenzyls with $B(C_6F_5)_3$ gives only ionic products, $[ZrCp_2(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$ **(17)** (Scheme 11, pathway C).[60] In this case the electron deficiency of the metal cation is partly alleviated by the η^2-co-ordination of the benzyl ligand, indicated spectroscopically by a high-field shift of *ca.* 30 ppm of the ^{13}C NMR resonance of the *ipso*-carbon of the phenyl ring, as well as characteristic changes in the C–H and H–H coupling constants of the benzylic CH_2 group. The NMR spectrum of $[ZrCp''_2(CH_2Ph)]^+[B(C_6F_5)_4]^-$ in toluene at 60 °C confirmed the stability of the η^2-benzyl bonding mode at higher temperatures, *i.e.* under polymerisation conditions [Cp'' = $C_5H_3(SiMe_3)_2$-1,3]. Several cationic benzyl complexes have been prepared; those with stereoselective ligands, such as *rac*-$[Zr(C_2H_4)Cp'_2(CH_2Ph)]^+$ (Cp' = indenyl), proved to be excellent propene polymerisation catalysts, with similar stereoselectivities but higher productivities than the corresponding *rac*-$[ZrCl_2(C_2H_4)Cp'_2]$–MAO catalysts.[61,62]

Not only arene substituents in benzyl ligands are able to displace a weakly co-ordinating anion from the co-ordination sphere. The reaction of the half-sandwich compounds [M-Cp'Me_3] [M = Zr or Hf; Cp' = C_5Me_5 or $C_5H_3(SiMe_3)_2$] with $B(C_6F_5)_3$ gives the toluene complexes **18**, whereas the zwitterionic complex **19** is only formed if M = Ti (Scheme 12).[63] Although it is debatable based on the structural parameters whether the toluene ligand in **18** is η^5 or η^6 bound, it is best understood as a 16-electron analogue of $[MCp_2Me_2]$ and is comparatively unreactive.[64] Achieving a metallocene-type structure by solvent complexation is evidently preferable to anion co-ordination, a good illustration that the solvent in electrophilic systems is not necessarily relegated to a spectator role.
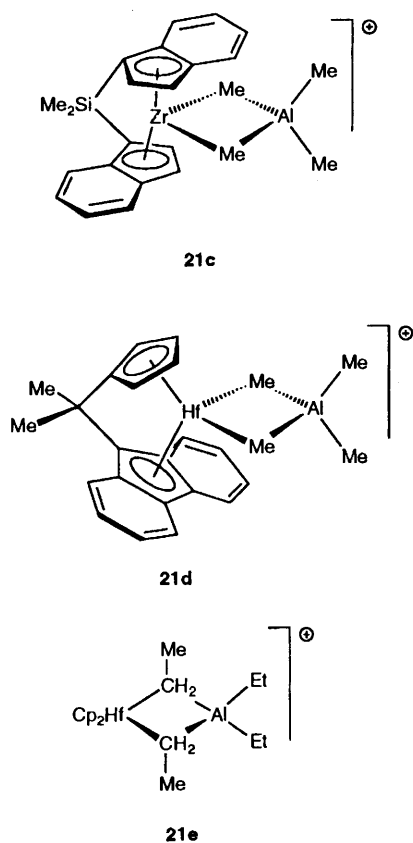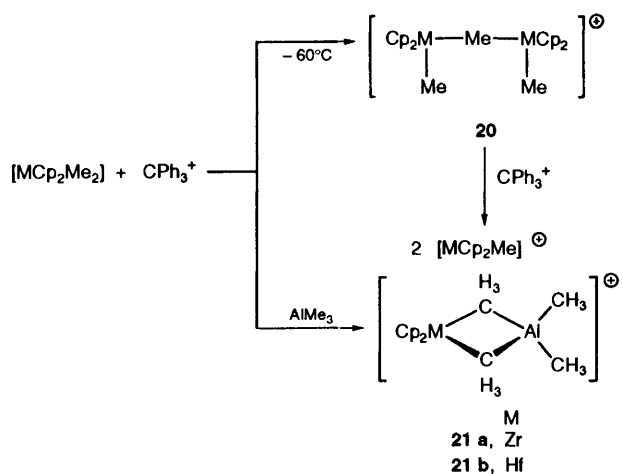
The η^2-benzyl ligand in **17** blocks the co-ordination site necessary for alkene binding during polymerisation. Nevertheless, complexes of type **17** are highly active; it is thought that they act as a reservoir for the active species, and that the first insertion is preceded by an $\eta^2 \rightarrow \eta^1$ rearrangement.[61] Such a reversible stabilisation in a way that does not poison the catalyst (unlike donor ligands) but allows it to participate in equilibria leading to the active species promises to be quite a general and useful facet of the chemistry of cationic metallocene alkyls; it helps to prevent the excessively high initial activity that would be expected if only 'pure' active species were present, and it may reduce decomposition and deactivation reactions. Neutral metal alkyls fulfil such a stabilising role. The reaction of $[ZrCp_2Me_2]$ with $[CPh_3][B(C_6F_5)_4]$ proceeds in stages. The first product formed at low temperature is a methyl-bridged dinuclear species, $[(ZrCp_2Me)_2(\mu$-Me)]^+$ **(20)** (Scheme 13). The stability of this species depends on the Cp ligands. Whereas the C_5H_5 complex reacts with further CPh_3^+ in CD_2Cl_2 even at -40 °C, the analogous $Me_2SiCp'_2$ (Cp' = indenyl) complex is stable in this solvent up to nearly 20 °C.[65] The formation of such dinuclear species has also been observed for cationic titanium[56] and thorium[57] complexes. In the system $[ZrCp_2Me_2]$–$B(C_6F_5)_3$ the co-ordination of excess $[ZrCp_2Me_2]$ to $[ZrCp_2Me]^+$ competes with the co-ordination of $[BMe(C_5F_3)_5]^-$ to give an equilibrium between **16** and **20**.[66]

Trimethylaluminium forms even more stable adducts with $[MCp'_2Me]^+$, leading to the heterodinuclear complexes $[Cp'_2M(\mu$-Me)_2AlMe_2]^+$ **(21, M** = Zr or Hf).[65] The formation of complexes **21** is essentially quantitative; typical examples are shown in Scheme 13 **(21a–21d)**. The complexes are isolable as microcrystalline solids or oils. The methyl coupling constants indicate that the CH_3 bridge in **20** is most probably approximately linear, with a trigonal bipyramidal carbon atom, while the Zr–CH_3–Al angle is acute, as in Al_2Me_6.

The facile formation of **20** and particularly **21** points to another way, apart from anion co-ordination, in which an active centre carrying a growing polymer chain can be transformed into a temporarily dormant species, in line with the 'intermittent growth' model (Scheme 3). Ethyl complexes, as models for species with longer polymer chains, form similar but less stable dinuclear compounds, as shown in the case of the hafnium complexes $[(HfCp_2Et)_2(\mu$-Et)]^+$ and $[Cp_2Hf(\mu$-Et)_2AlEt_2]^+$ **(21e)**. Evidently the tendency for dinuclear species to dissociate increases with increasing alkyl chain length.[67]

It is evident from the mechanistic considerations that neither **20** nor **21** possess the vacant co-ordination sites required for monomer binding and chain growth. Nevertheless, the fact that these complexes are extremely active catalysts can be accommodated by postulating a dissociation equilibrium which generates a common catalytically active species $[ZrCp_2Me]^+$, from both **20** and **21**. If so, the productivity of the catalyst should decrease as the concentration of the neutral metal alkyl increases, *i.e.* as the equilibrium is shifted towards the dinuclear compounds (Scheme 14). This is indeed observed; for example, the propene polymerisation activity of the catalyst system *rac*-$[Zr(Me_2SiCp'_2)Me_2]$–$[CPh_3][B(C_6F_5)_4]$ (Cp' = indenyl) decreases with increasing $Zr:Ph_3C^+$ ratio, and if $AlMe_3$ is added, with increasing $Al:Zr$ ratio. The effect is quite pronounced at 20 °C but still noticeable at polymerisation temperatures of 60 °C when dissociation is favoured. The highest productivities are obtained at an $Al:Zr$ ratio of 1:1 (Fig. 1). The catalyst productivity increases further when $AlMe_3$ is replaced by $AlEt_3$, in line with the more facile dissociation of $AlEt_3$ adducts.[65,67]

The formation of **21** provides a mechanism for the transfer of alkyl chains from the transition metal to aluminium. As a consequence, high concentrations of aluminium alkyls not only suppress catalytic activity but also reduce the polymer molecular weight. Under the conditions given in Fig. 1, the M_w

Scheme 13

these sterically very shielded anions are less co-ordinating than $[B(C_6F_5)_4]^-$ and give higher polymer molecular weights, there is NMR evidence for the formation of tight ion pairs and anion co-ordination *via* fluorine contacts.[68]

There has been considerable speculation in the past about the interaction of MAO with metallocenes and its mode of activation. Equilibria such as **22a–22b** have been suggested, and complex **23** was isolated which can be seen as a model for the co-ordination of $[ZrCp_2Me]^+$ to an Al–O–Al bond of MAO.[69,70] The interaction of solid, essentially tri-methylaluminium-free MAO with $[ZrCp_2(^{13}CH_3)_2]$ provides evidence for the formation of a cation-like zirconium methyl species in MAO-activated catalysts, with a methyl ^{13}C chemical shift close to that of **16** or $[ZrCp_2Me]^+$ in solution.[71] The data do not, unfortunately, permit the distinction between 'unassociated', methyl-bound or oxygen-bound $[ZrCp_2Me]^+$. As discussed in the introduction, MAO exists in solution as a mixture of equilibrium species including significant amounts of Al_2Me_6, and it seems most likely that under these conditions heterobinuclear $AlMe_3$ adducts of type **21** are the primary products of MAO activation.[65]

Whereas the existence of cationic 14-electron metallocene alkyls $[MCp_2R]^+$ and their reactivity is by now fairly well documented, there is considerably less information about the olefin π complex that precedes the alkyl migration step (*cf.* Scheme 4). In 1974 Tebbe and co-workers described the niobium(III) complex $[NbCp_2Et(C_2H_4)]$ which possesses some of the requirements for a structural model for the π complex but, as a d^2 compound, exhibits extensive back-bonding and short Nb–C bonds which would not be present in a d^0 zirconium(IV) complex.[72] Horton's dienyl complex **24**[73] and the alkoxy complexes **25**[74] give a useful indication of the zirconium–alkene bond distances involved and hence the strength of this interaction.

24   **25**
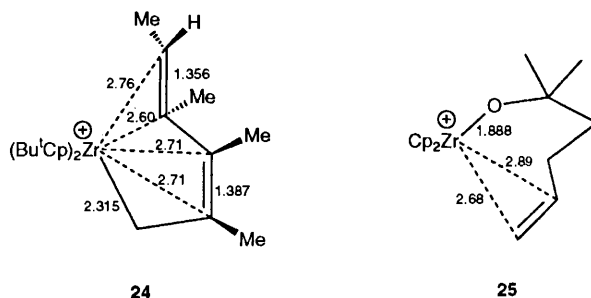
Stereoselective Propene Polymerisation

As Natta discovered, heterogeneous polymerisation catalysts polymerise propene with a very high degree of stereoselectivity. It is thought that polymerisation takes place at the edge of a $TiCl_3$ crystal. The titanium centres are octahedrally co-ordinated; in the active species one of these co-ordination sites is occupied by the polymer chain, a second by the monomer. Stereoselectivity results because a neighbouring Cl atom (Cl* in structure **26**) restricts the rotation of the polymer chain. The monomer then binds to Ti such that steric interaction with the chiral β-carbon of the alkyl chain is minimised (*si* co-ordination in **26a**) whereas co-ordination of the other π-face (**26b**) is disfavoured. The result is highly isotactic polypropene; the regular structure is reflected in a high melting point (165 °C) and high stiffness and hardness.

Propene can be polymerised with varying degrees of stereo-control. Atactic polypropene (aPP) has a random orientation of methyl groups along the chain, lacks crystallinity and is usually an oil or wax. In isotactic polypropene (iPP) all methyl groups show the same orientation so that the polymer strands can align themselves to give crystalline domains. In hemi-

value of polypropene is more than halved as the Al–Zr ratio is increased from 1:1 to 100:1.[65]
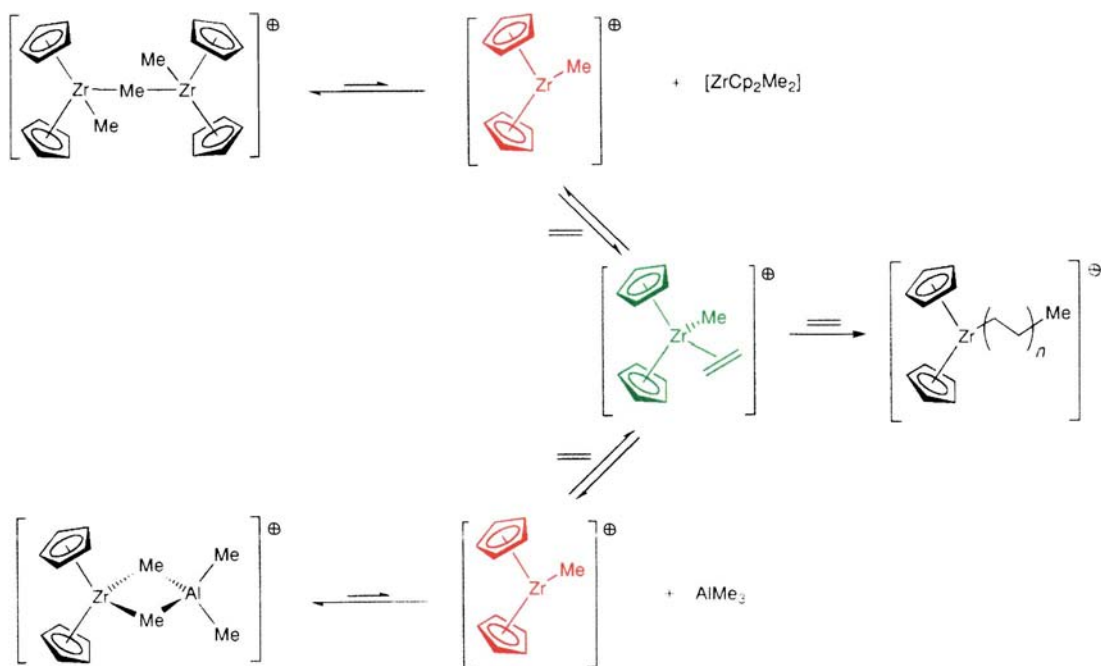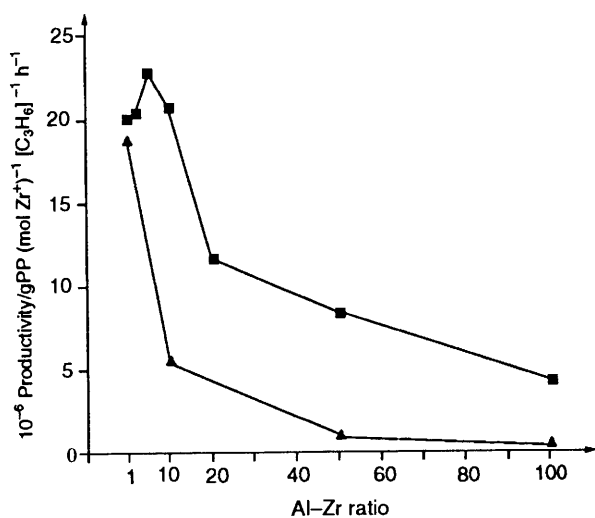
Commonly used metallocene catalysts require of course rather high concentrations of aluminium alkyls in order to attain acceptable productivity levels. The aluminium component plays several important roles: as alkylating agent, as Lewis acid, as a provider of counteranions, as a scavenger and as stabiliser of the active species. As the discussion above shows, appropriate separation of these functions leads to well defined catalyst systems which require no or very low concentrations of aluminium alkyls.

The discussion above illustrates that 14-electron cationic complexes such as the 'active species' $[ZrCp_2Me]^+$ are rather elusive and best prepared *in situ*. The closest approach so far to 'non-stabilised' $[ZrCp_2R]^+$ was reported recently by Marks and co-workers[68] who showed that the highly hindered anions $[B(C_6F_4SiR_3)_4]^-$ ($R_3 = Pr^i_3$ or Me_2Bu^t) form isolable salts with $[ZrCp'_2Me]^+$ (Cp' = C_5H_5 or $C_5H_3Me_2$-1,2). Although

Scheme 14

Fig. 1 Propene polymerisation productivity of a $[Zr(Me_2SiCp'_2)\text{-}Me_2]\text{-}[CPh_3][B(C_6F_5)_4]\text{-}AlR_3$ (Cp' = indenyl) catalyst as a function of the Al-Zr ratio, R = Me (▲) or Et (■); toluene, 1 bar propene, 20 °C
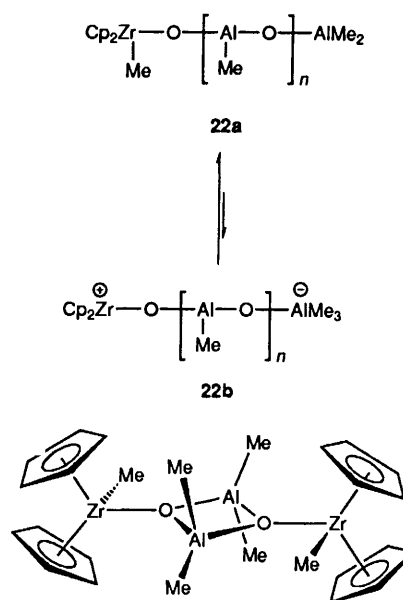
isotactic PP the orientation of every second methyl group is random, while in syndiotactic PP (sPP) the methyl orientations alternate (Scheme 15). Of these, only iPP and, to a more limited extent, aPP have found commercial uses at present.[45]

Isotactic polymer is produced when the monomer molecules in sucessive insertion steps bind to the metal *via* the same enantioface [either *re*, *re* or *si*, *si*, Scheme 15(a)], while co-ordination to the opposite enantioface in every second insertion step leads to sPP.

Metallocene catalysts can achieve this stereocontrol in two ways. Ewen showed in 1984 that [TiCp$_2$Ph$_2$]–MAO catalysts produce iPP at low polymerisation temperatures (– 50 °C) with the stereochemistry of the insertion step being controlled by the chiral β-carbon of the growing chain (Scheme 16).[75] This leads to a polymer in which a stereoerror is perpetuated and not corrected ('chain end control', **27a**). By contrast, a ligand framework with C_2 symmetry, as in **28**, leads to a polymer

where a misinsertion is corrected ('enantiomorphic site control', **27b**).[76]

The stereoselective propene polymerisation has recently been reviewed in some detail,[36] and only the most pertinent aspect will be addressed here. As the example of [TiCpPh$_2$]–MAO showed,[75] a rigid ligand framework (*e.g.* **28**) is in principle not necessary for stereocontrol but indispensable for polymerisation at usual temperatures (> 50 °C). The hindered rotation of monosubstituted Cp ligands provides a measure of stereocontrol by imposing C_2 symmetry on the metallocene. An interesting variation of stereocontrol with temperature was found for [Ti(C$_5$H$_4$Pr^i)$_2$Ph$_2$]–MAO which produces predominantly isotactic polypropene at – 50 °C, nearly atactic polymer at – 10 °C and polymer with an increased

syndiotactic component at +10 °C, as a result of subtle changes in the preferred olefin co-ordination over this temperature range.[77] Hindered rotation is also the reason why [ZrCl$_2$Cp'$_2$] (Cp' = 1-methylfluorenyl) gives predominantly isotactic polymer.[78] The main attraction of these comparatively simple Cp derivatives is the ease of their synthesis. However, neither stereoselectivities nor polymer molecular weights can rival the results of heterogeneous catalysts.[79]

A significant breakthrough was made with C_2 symmetric, fairly rigid *ansa*-metallocenes of type **28** and **29**.[80] The ligand framework imposes an insertion stereochemistry as outlined in Scheme 15(*a*) and gives very highly active catalysts, although here, too, both molecular weight and stereoregularity (and hence physical properties) of the polymer left room for improvement.[76] For some years there was an extensive search

for new improved ligand systems. A judicious choice of substituents on both the C_5 and the C_6 ring of the indenyl skeleton proved to be the key to success, *e.g.* **30** and **31**.[81,82] Restricting the co-ordination sphere of the metal in this way did not only improve the stereoselectivity but resulted in a dramatic increase in the polymer molecular weight and catalyst productivity as well. For example, **30** (R = 1-naphthyl) matches heterogeneous catalysts in polymer molecular weight (*ca.* 900 000) and tacticity but it is about 40 times more active.[81] It appears that **30** and **31** represent something like an endpoint in ligand development for stereoselective polymerisation at present.

ansa-Metallocenes with Cp derivatives of very different sizes and C_s symmetry, as in **32**, impose a polymerisation stereochemistry as in Scheme 15(*b*) and give syndiotactic polypropene.[83] In fact, this ligand system proved to be remarkably versatile; the introduction of a methyl or *tert*-butyl substituent on the cyclopentadienyl ring changed the stereocontrol of every second insertion step sufficiently to lead to hemiisotactic and isotactic polymer, respectively (Scheme 17).[84] Elastomeric polypropene with isotactic and atactic blocks have been prepared with **33** and **34**.[85,86]

Closer inspection of the stereoselectivity of propene polymerisation with *ansa*-metallocenes has shed light on the mechanism by which the ligand framework controls the polymer structure. Surprisingly, the insertion of propene into [Zr(C$_2$H$_4$)Cp'$_2$Me]$^+$ (Cp' = indenyl) proceeds in a non-stereoselective manner, insertion into a Zr–Et bond, however, is

26a   26b

hemiisotactic PP   atactic PP
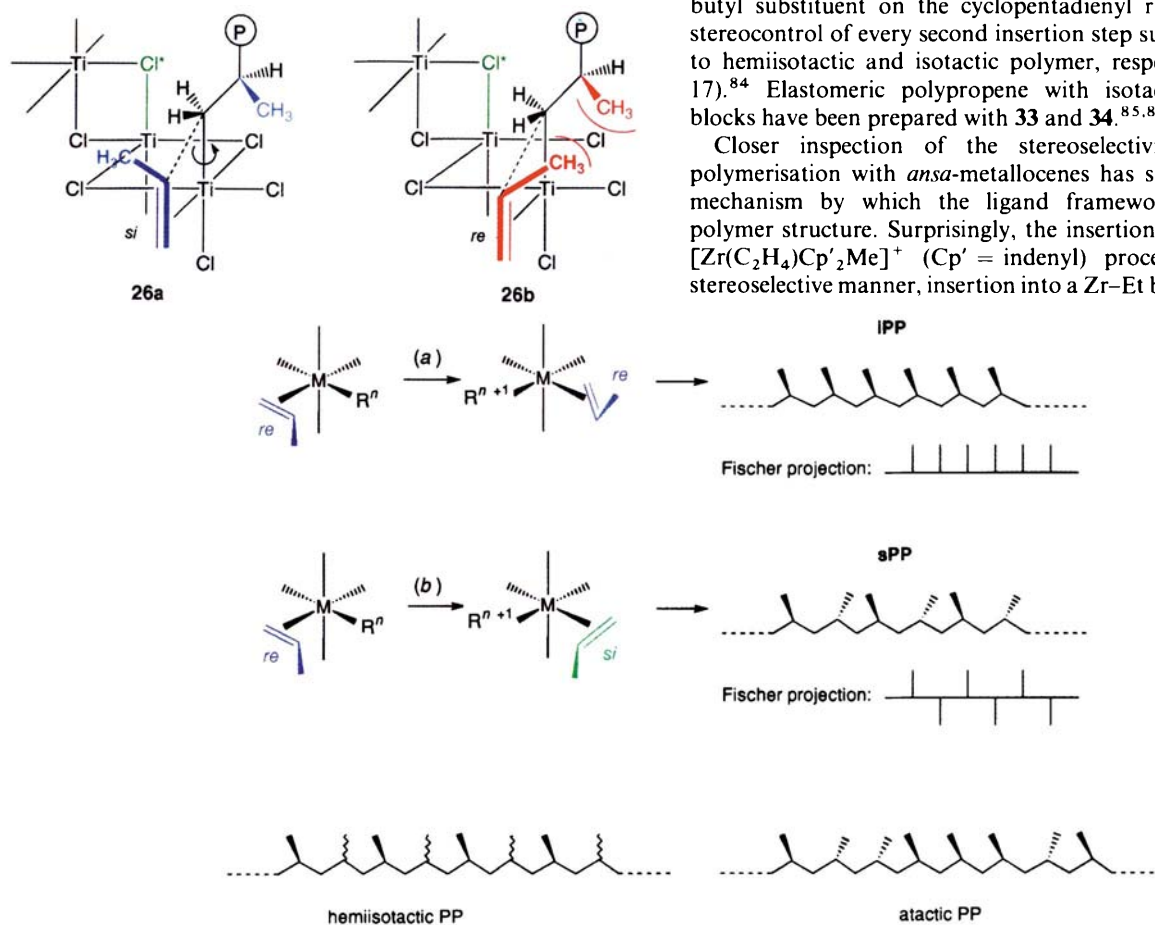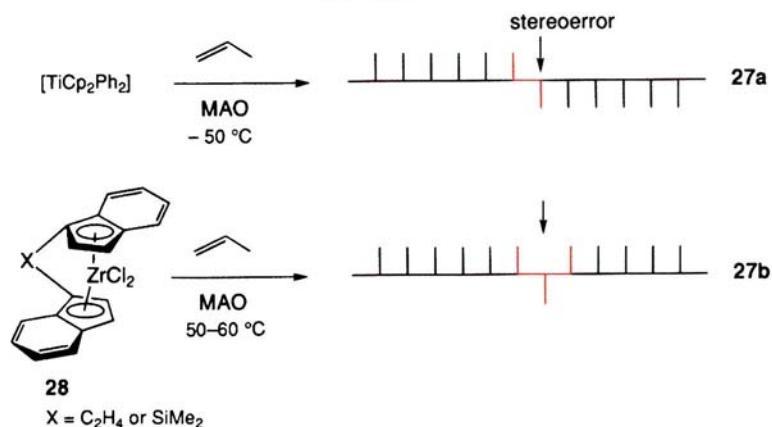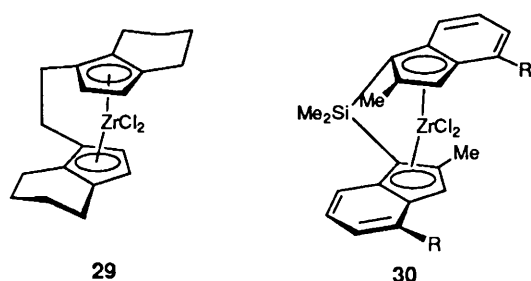
Scheme 15

Scheme 16

highly selective.[87] According to molecular mechanics calculations by Corradini and co-workers.[88] the ligand framework does not influence the enantiofacial orientation of the monomer directly but controls the conformation of the alkyl ligand, hence the effect is only noticeable if the alkyl chain carries at least two carbons. The incoming monomer then co-ordinates preferentially with whichever orientation minimises repulsive van der Waals interactions with the alkyl ligand.

Occasionally mis-insertions occur, and a propene molecule produces a 2,1- rather than the 1,2-insertion product, leading to a secondary alkyl chain end (Scheme 18). Whenever this happens any subsequent insertion, either 1,2 or 2,1, becomes difficult. The situation is resolved by a (comparatively slow) β-H elimination step which can lead to isomerisation and further chain growth with a 1,3-insertion defect, or to the start of a new polymer chain. As a result, up to 90% of the potentially active zirconium species may be temporarily dormant because of 2,1-misinsertions.[89]

The relatively long-lived nature of 2,1-insertion products may also explain the apparent paradox that sterically highly congested complexes such as 30 or 31 not only give polymers with much better stereoregularity and much higher molecular weight than 28, but are also significantly more active. Evidently the substituents help to enforce the correct stereochemistry of monomer co-ordination; the 2-methyl substituents of the indenyl ring in particular guard against a monomer orientation that would lead to a 2,1-insertion product.
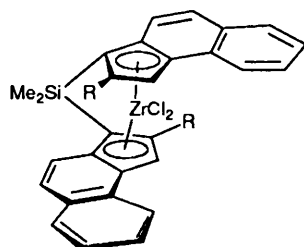
Comparison with Lanthanide Catalysts

Cationic Group 4 complexes of the type [MCp₂R]⁺ are isoelectronic with neutral metallocene complexes of the

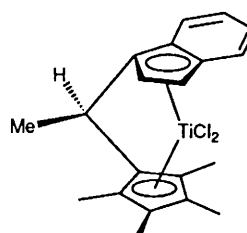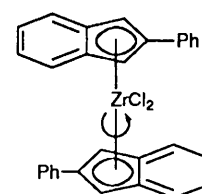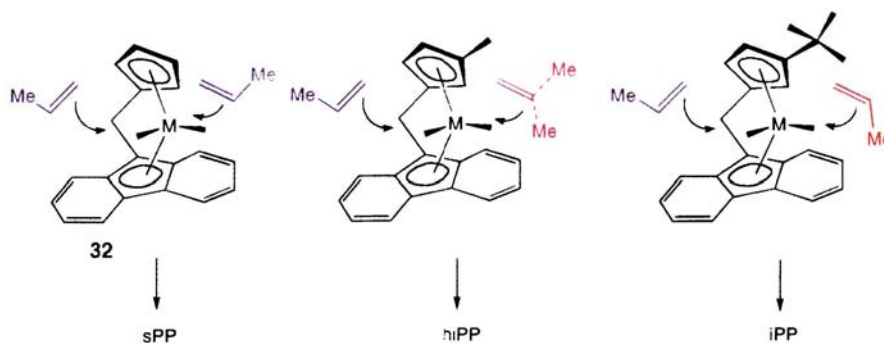lanthanide metals, [LnCp₂R]. The chemistry and reactivity of both groups of metals should therefore be quite similar, and the question arises why the comparatively simple lanthanide systems, which are mostly isolable and free of complications such as counteranions, should not be used in preference to Group 4 metals.

There are indeed many similarities. In the 1970s, the groups of Lappert, Ballard and co-workers[90] obtained methyl-bridged lanthanide–aluminium complexes [Cp₂Ln(μ-Me)₂AlMe₂] (35) (Ln = Sc, Y, Gd, Dy, Ho, Er, Tm or Yb) which are analogous to the cationic binuclear Zr and Hf complexes 21 reported recently.[65] These lanthanide complexes are thermally remarkably stable and may be purified by sublimation. A short time later Watson showed that [LuCp*₂Me] polymerised ethylene at a high rate but gave a simple insertion product with propene, [LuCp₂*(CH₂CHMe₂)], which reacted with hydrogen under hydrogenolysis to yield [LuHCp₂*], all steps of relevance to Ziegler catalysis.[91] The hydrogenolysis of isolable lanthanide alkyls was employed effectively by Marks and co-workers in order to convert the inactive alkyls [LnCp₂*{CH(SiMe₃)₂}] (Ln = La, Nd or Lu) into the hydrides [LnHCp*₂] which are highly active, if short lived, ethylene polymerisation catalysts.[92] Similar neodymium catalysts have been used to polymerise ethylene under very high pressure and temperatures in tube reactors (200 °C, 1200 bar) where the short catalyst lifetimes pose no disadvantage.[93]

As the early studies showed, a major difference between lanthanide and Group 4 metal catalysts is the failure of the former to polymerise alk-1-enes. There are also structural differences. Recent calculations showed that the ground-state geometry of [ZrCp₂Me]⁺ is pyramidal (36) while complexes of trivalent metals such as scandium and lanthanides are trigonal planar (37),[28] i.e. the geometry of 36 is better adapted for olefin co-ordination. In contrast to the somewhat elusive cation 36 many complexes of type [LnCp′₂Me] are isolable; they form μ-CH₃ bridged dimers easily, provided the steric bulk of Cp′ allows it.[94]

This propensity to form stable dimers is one feature that distinguishes lanthanide complexes from the Group 4 cations. Although dimeric hydrides [(LnHCp*₂)₂] are excellent hydrogenation catalysts,[92] it could be shown that a μ-H ligand reacts with olefins 10⁸–10¹⁰ times more slowly than a terminal hydride. For example, 38 reacts with alk-1-enes only slowly to give remarkably stable μ-alkyl complexes of type 39; there is no

29   30

31   33   34

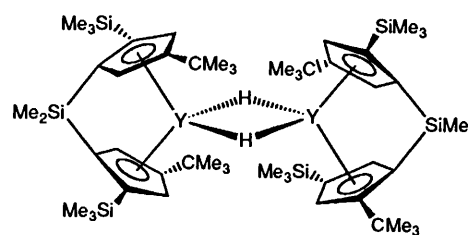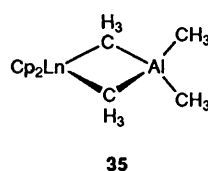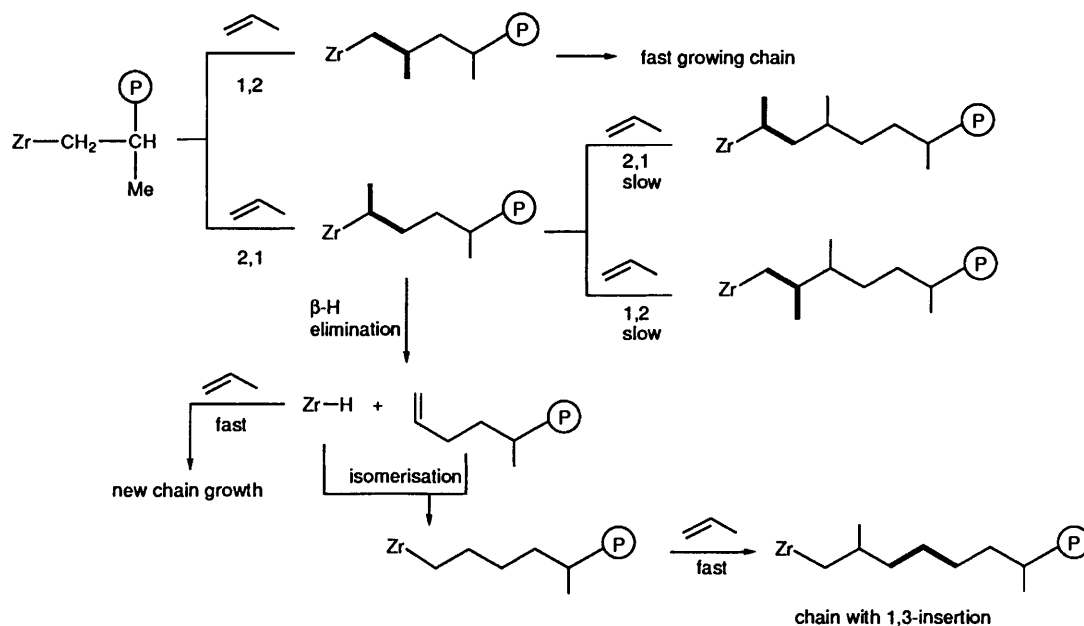
32

sPP   hiPP   iPP

Scheme 17

Scheme 18

fast growing chain

1,2

2,1

2,1
slow

1,2
slow

β-H
elimination

fast

new chain growth

isomerisation

chain with 1,3-insertion

Zr—CH₂—CH
      |
      Me

Zr—H +

35

Cp₂Ln, Al with CH₃ groups, H₃C bridges

40

36   **37**

Me⁺   Me

x   x

y   y

Me₂Si, Ln—CH(SiMe₃)₂

Ln = Y or Lu

H₂

38

39
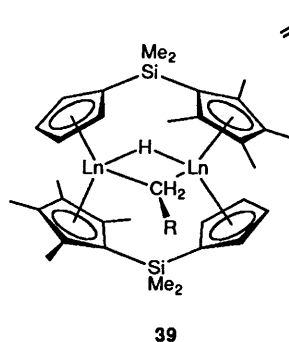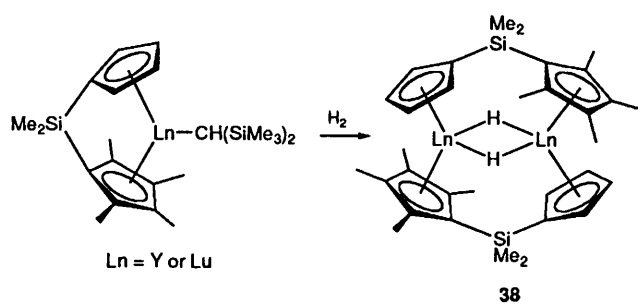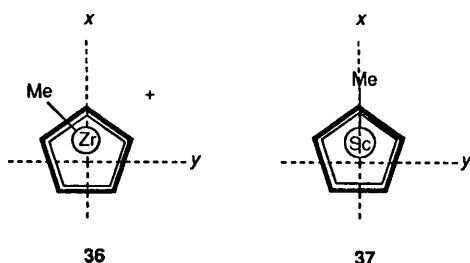
Scheme 19

further reaction, and even the hydrogenolysis of **39** is rather slow (Scheme 19).[95] The closely related aryloxide complex [{Y(μ-H)Cp*(OC₆H₃Buᵗ₂-2,6)}₂] shows similar behaviour. Bridging hydrides are evidently preferred over μ-aryloxo ligands, and although ethylene is polymerised rapidly, propene inserts only once to give a [Y₂(μ-H)(μ-CH₂CH₂Me)] complex which is stable to β-H elimination.[96] The ability to form stable μ-alkyl compounds must inevitably lead to catalyst deactivation. Nevertheless, the dimeric hydride **40** does polymerise alk-1-enes from propene to hexene to give polymers of moderate molecular weight, albeit over a period of several days.[97]

Another distinguishing feature of lanthanide chemistry is the propensity to undergo C–H activation rather than insertion ('σ-bond metathesis'). Thus [ScCp*₂Me] exchanges methyl groups with methane, reacts with arenes to give metal aryls, and activates styrenes to give vinyl complexes. One molecule of propene is inserted, a second molecule reacts with σ-bond metathesis (Scheme 20).[98,99] None of these reactions have so far been demonstrated for Group 4 metal alkyls.

Catalyst Deactivation Reactions

Metallocene dihalide–MAO catalysts show a more or less rapid exponential decay in activity in the initial phase of polymerisation before stabilising at a lower level. With cationic metal alkyl catalysts the initial activities are usually very high, with an even more rapid decay. Catalyst deactivation is clearly an important consideration for any commercial use of these systems. However, there is so far very little information about possible deactivation pathways.

In early work Kaminsky et al.[100] succeeded in isolating a number of ethylene-bridged complexes from the reaction of

[ZrCp$_2$Et(Cl)] with AlEt$_3$ which were thought to be side-products, e.g. **41** and **42**.

Fischer and Mülhaupt determined the kinetics of catalyst deactivation for the atactic polymerisation of propene with [ZrCl$_2$Cp$_2$]–MAO catalysts.[101] A reversible and an irreversible deactivation step could be distinguished, both second order in [Zr]. Although it is not possible to derive firm conclusions about the nature of the deactivated species from such measurements, it is tempting to think that the reversible deactivation step consists of the formation of alkyl-bridged dinuclear zirconium complexes of type **20**.

Other potential deactivation pathways are the formation of dinuclear species by α- or β-CH activation. The chemistry of cationic Group 4 alkyls provides examples of both. The fulvalene complex **43** reacts with CPh$_3$$^+$ or B(C$_6$F$_5$)$_3$ even at −60 °C with immediate elimination of methane to give a
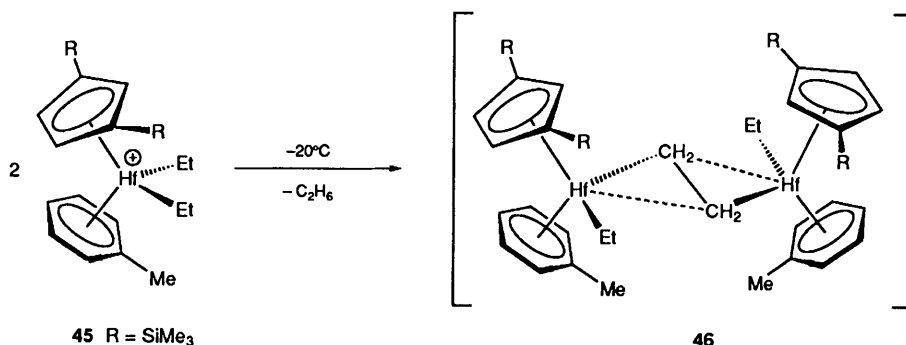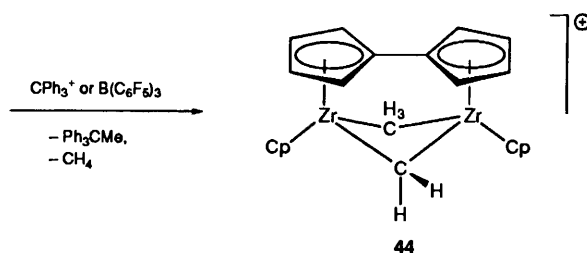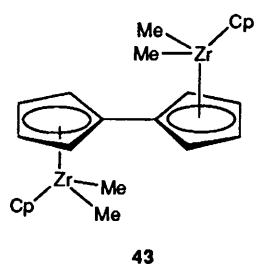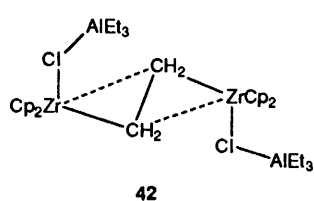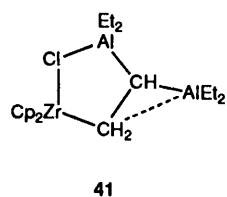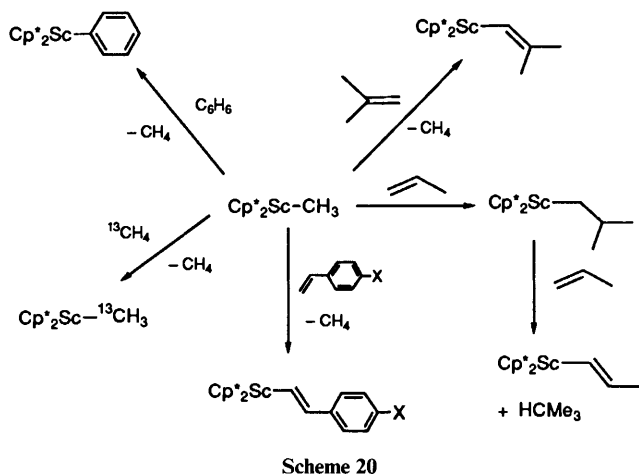
relatively inactive μ-CH$_2$ complex **44**,[102] and the hafnium ethyl complex **45** decomposes slowly with elimination of ethane to give **46** (Scheme 21), a compound reminiscent of **42**.[64] The neutral dicarbollide complex [{ZrCp*(C$_2$B$_9$H$_{11}$)Me}$_n$] also decomposes via α-H elimination to a stable μ-CH$_2$ product, albeit at a much higher temperature than **43** (45 °C, 2 h).[103]

Cationic complexes containing [B(C$_6$F$_5$)$_4$]$^-$ and related counteranions may be expected to be prone to deactivation by aryl or fluoride transfer, although there is at present no evidence for this under catalytic conditions. Such reactions do, however, occur slowly at room temperature and above. For example, the reaction of **47** with B(C$_6$F$_5$)$_3$ in benzene over 24 h gave **48**, (Scheme 22)[104] and similarly **16** (Scheme 11) was found to slowly form the fluoride complex [(ZrCp'$_2$Me)$_2$(μ-F)]-[MeB(C$_6$F$_5$)$_3$].[59b]

Alternative Catalysts and Ligand Systems

As the work described above has documented, cyclopentadienyl complexes possess almost ideal catalytic properties. Nevertheless, increasing efforts are being made exploring the potential of new ligand environments and catalyst types. The aim is twofold: first, to find a ligand system that can rival or even better the extensively patented Cp compounds, and second, to eliminate the complications of a counteranion and to develop neutral analogues of cationic complexes.

Chelating cyclopentadienyl–amide ligands as in **49** and **50** have proved very successful in a range of polymerisations and co-polymerisations.[105,106] Benzamidinato complexes such as **47** catalyse the polymerisation of ethylene but are less active towards propene.[107] A more radical departure from the cyclopentadienyl theme are macrocycles such as **51** and **52**. Although the zirconocene dialkyls with these ligands have a geometry closely similar to cyclopentadienyl complexes and cationic alkyl derivatives can be made, the catalytic activity of these complexes are at best modest.[108] The Schiff-base complexes **53**, too, are poor polymerisation catalysts.[109] Tridentate amide complexes have also been prepared, e.g. **54**.[110] Bidentate aryloxides afford a series of metal halide and alkyl complexes, e.g. **55** and **56**. In the presence of MAO some of these complexes are moderately active as ethylene polymerisation catalysts. Unlike metallocene catalysts these complexes give polymers with a rather broad molecular weight
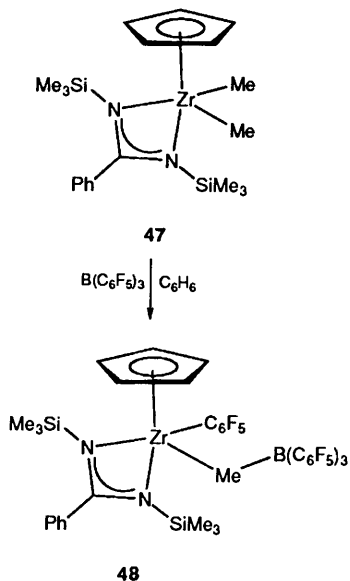

Scheme 20

41   **42**

43   **44**

45 R = SiMe$_3$ **46**

Scheme 21

distribution (M_w/M_n = 7–24), and it is not certain whether the identity of the complexes remains intact under polymerisation conditions.[111]

An alternative method to the generation of cationic catalysts from metallocene dialkyls has recently been developed by Erker and co-workers who prepared zwitterionic alkyl complexes by attack of $B(C_6F_5)$ on zirconium(II) and hafnium(II) diene complexes (Scheme 23). They catalyse the polymerisation of ethylene and propene.[112] Marks and co-workers, used a similar strategy to convert titanium–diene complexes of type 49 (X_2 = diene) into highly active catalysts for ethylene–oct-1-ene copolymerisations.[113]

The replacement of a Cp ligand in the cation $[MCp_2R]^+$ by a dianionic ligand (L) generates an electroneutral analogue, $[MCp(L)R]$, a potentially useful strategy in order to eliminate the counteranion influence and to evaluate the role of the positive charge on the metal. The first attempts in this direction were made by Jordan and co-workers who used the $[C_2-B_9H_{11}]^{2-}$ carboranyl dianion. The compound $[\{ZrCp^*(C_2B_9-H_{11})Me\}_n]$ is a polymer which shows moderate activity for ethylene polymerisation and oligomerises propene.[103] The thermally sensitive titanium derivative is even less reactive and dimerises ethylene very slowly to butene.[114] Other dianionic

ligands, such as trimethylenemethane and borolene $[C_4H_4-BX]^{2-}$ (X = NPr^i_2), afford the anionic complexes 57 and 58, respectively. With MAO as an activator 57 polymerises ethylene. In neither case have the neutral alkyl complexes $[ZrCp^*(L)R]$ been isolated.[115,116]

In both 57 and 58 the lithium countercation co-ordinates strongly to the chloride ligands, no doubt as the result of the accumulation of electron density on the metal due to the presence of doubly negatively charged π ligands. Such a reduction in the Lewis acidity of the metal centre is unlikely to be helpful to catalysis. An alternative is the use of cyclopentadienyl ligands with negatively charged substituents, $Cp^- - Z^-$. A series of complexes with Z = $B(C_6F_5)_3$ has been prepared according to Scheme 24 in which the counteranion is associated with the borato substituent and not co-ordinated to halide.[117] The dihalides 59 in the presence of MAO are highly active and produce high-molecular-weight polyethylene, as do catalysts generated from the dimethyls 60, $[CPh_3][B(C_6F_5)_4]$ and $AlBu^i_3$. The reaction of 60 with CPh_3^+ in the presence of $AlMe_3$ affords the highly hydrocarbon-soluble zwitterionic complex 61. Systems of this kind offer promise as a route to single component polymerisation catalysts which can be employed without the need for activators.

47

B(C₆F₅)₃ | C₆H₆

48

Scheme 22

Scheme 23

57   58

49   50   51   52
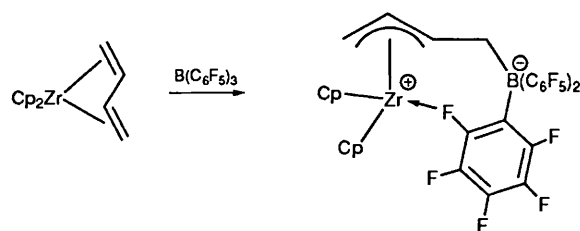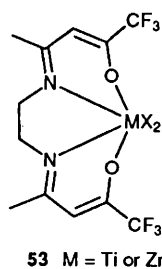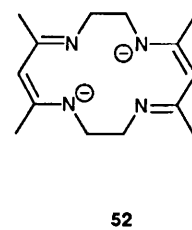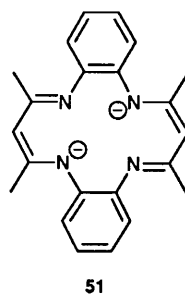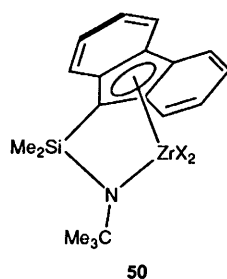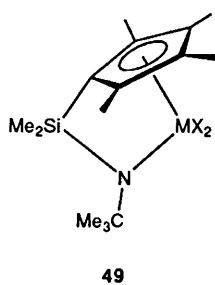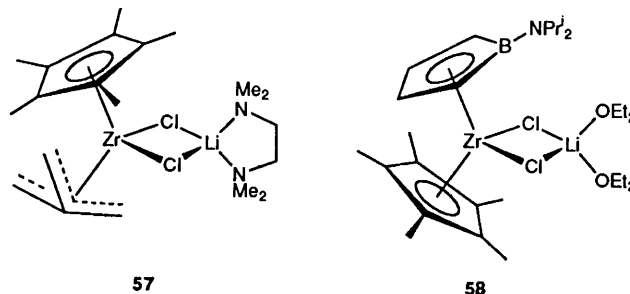
53 M = Ti or Zr   **54** R = SiMe₃   **55**   **56**

Scheme 24
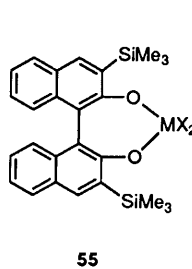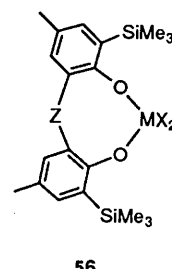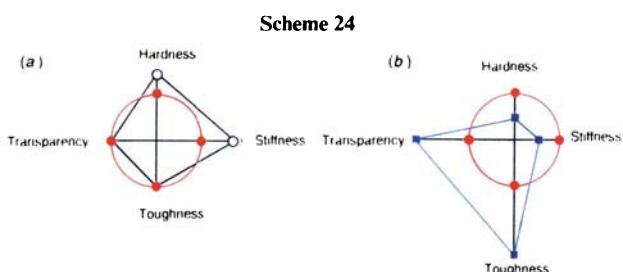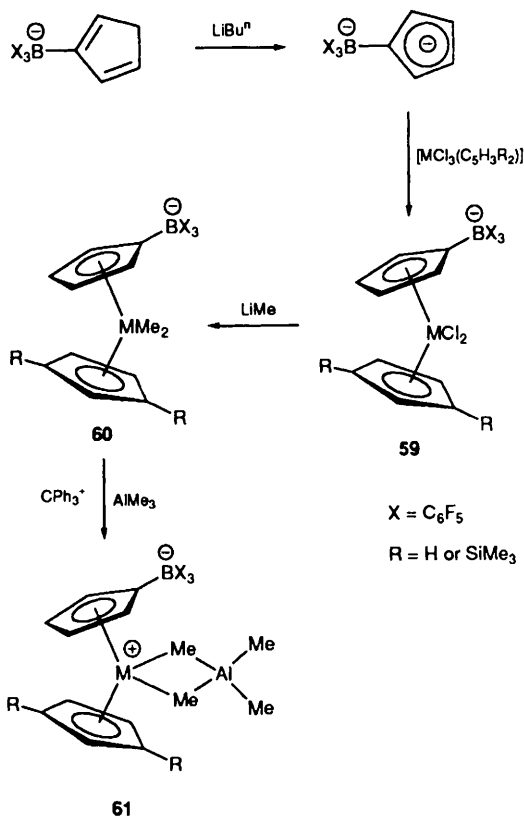
Fig. 2 Comparison of the properties of isotactic polypropene made with a heterogeneous catalyst (●) with the properties of (a) metallocene-derived isotactic polypropene (○), and (b) syndiotactic polypropene (■)

Outlook

The last decade has seen rapid progress in the understanding of metallocene-catalysed olefin polymerisations, and the mechanistic principles are now widely accepted. The emergence of metallocenes from the 'black-box era' of ill-defined catalyst brews was made possible by the rational application of fundamental concepts of organometallic reaction pathways and bonding modes, such as agostic interactions. Ligand design and reaction conditions can now be tailored to give a predetermined stereochemistry and, to a more limited extent, a particular activity or polymer molecular weight.
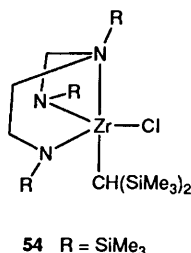
One of the main advantages of metallocene catalysts is their versatility. Polymer properties can be varied within wide limits to provide not just substitutes but alternatives to currently available polymers made with heterogeneous catalysts. It is the combination of various properties that is of interest to the polymer user, and these can vary widely for structurally closely related polymers made by different routes, as shown diagramatically in Fig. 2.[46]

The discussion above has concentrated primarily on the polymerisation of ethylene and propene. Metallocenes and related complexes are of course applied much more widely, such as in ethylene–alk-1-ene copolymerisations, the (syndiotactic) polymerisation of styrene, the cyclic polymerisation of 1,5-dienes, the polymerisation and block-copolymerisation of methacrylates, and in the copolymerisation of ethylene with norbornene to give highly transparent polymers with interesting speciality optical and medical applications.

Although the control of stereoselectivity in propene polymerisations has been a major focus of interest in the past 10 years, not least in industrial research laboratories, these complexes with their quite sophisticated ligand environments do not yet appear to have been introduced in large-scale processes (however, there is optimism[3]). Syndiotactic polypropene, too, has not yet found its niche. It is in non-stereoselective copolymerisations that metallocenes proved their worth most and found applications most readily, the major advantage of even simple C_5H_5 complexes being their ability to uniformly incorporate higher alk-1-enes into a polyethylene chain, independent of the polymer molecular weight. These catalysts can be supported on MAO-coated silica (thereby reducing the Al–Zr ratio to a tolerable 200–300 : 1) and retrofitted into existing plants. Tens of thousands of tons of metallocene-derived linear low-density polyethylene (LLDPE) are already being produced in this way. The industrial interest is reflected in the number of patent applications for metallocene catalysts which has risen worldwide from only two in 1982 to over 600 in 1993.[46] The chemistry of catalyst-support interactions in these heterogenised metallocene catalysts is not yet well understood. No doubt this will be an important focus of interest in years to come.

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