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Anion Influence in Metallocene-based Olefin Polymerisation Catalysts

*Polly A. Wilson, Mark H. Hannant, Joseph A. Wright, Roderick D. Cannon, Manfred Bochmann**

Summary: The effects of perfluoroarylborate anions on the activities of metallocene-based propylene polymerisation catalysts on the one hand, and on the cationic polymerisation of isobutylene to butyl rubber are summarised. In both systems the anions follow the same activity sequence, $[CN\{B(C_6F_5)_3\}_2]^- > [H_2N\{B(C_6F_5)_3\}_2]^-] \approx [B(C_6F_5)_4]^- > [MeB(C_6F_5)_3]^-$. In an effort to maximise the delocalisation of negative charge over large volumes, new anions based on the very bulky borane $B(C_6F_4\text{-}2\text{-}C_6F_5)_3$ (PBB) with longer linking groups have been prepared, e.g $[N(CN\text{-}PBB)_2]^-$. The van der Waals volumes of representative anions and cations are reported. The influence of anions on the structure of catalytically active species is demonstrated using $(SBI)Zr(CH_2SiMe_3)(\mu\text{-}Me)B(C_6F_5)_3$ and $[(SBI)Zr(CH_2SiMe_3)^+ \cdots B(C_6F_5)_4^-]$ as examples. The alkyl ligand in the latter is stabilised by agostic bonding, which relegates the anion into the outer coordination sphere. The differences in ion pair structure profoundly influence the nature of chain termination in 1-hexene polymerisations: whereas the $MeB(C_6F_5)_3^-$ catalyst gives a mixture of vinylene and vinylidene terminations, with the latter predominanting at higher temperatures and conversions, the $B(C_6F_5)_4^-$ system terminates exclusively after 2,1-misinsertion to give vinylene-terminated poly(1-hexene).

Keywords: catalysis; cationic polymerisation; metallocene catalysts; microstructure; polyolefins

Introduction

It is now well established that in group 4 metal catalysts ion pairs of the type $[Cp^R{}_2M\text{-}R]^+X^-$ act as the catalytically active species in olefin polymerisations.[1–5] In these ion pairs, the greater or lesser coordination ability of X^- determines the Lewis acidity of the metal centre and hence its ability to bind monomer molecules, while the ligand framework is primarily responsible for the regio- and stereo-selectivity of the chain growth process. Early mechanistic proposals relegated the anion largely to a spectator role: it was assumed that the ion pair dissociated in solution to generate the active 14-electron species $[Cp^R{}_2M\text{-}R]^+$, and that all catalytic processes only involved this cation.[1,2] Indeed, the stereoselectivity of 1-alkene polymerisations with C_2- and C_s-symmetric metallocenes can be elegantly explained taking only the cationic species into account.[3]

Nevertheless, the activity of a catalyst depends very strongly on the nature of X^-, and it is therefore not surprising that a lot of effort has been spent on “anion engineering”. The most successful anions, in terms of chemical stability combined with high catalytic activity, are based on the perfluorophenylborate motif (Chart I); for leading references see a recent review.[4]

Results and Discussion

Anion nucleophilicity is reduced if the negative charge can be delocalised over as

Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, UK

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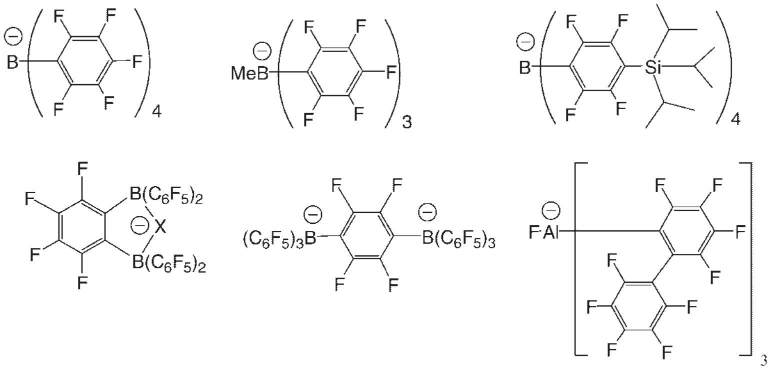

Chart I.

large a volume as possible. This aim is realised by the conceptually simple method of constructing anions by coordinating strongly Lewis acidic $B(C_6F_5)_3$ to an anionic linker, such as CN^- and NH_2^- (Chart II).[6,7] Catalyst activators based on such anions are capable of producing drastic increases in catalyst activity; highlighted for example by our observation some time ago that $(SBI)ZrMe_2$ catalysts activated with TIBA/$CPh_3[(C_6F_5)_3BCNB(C_6F_5)_3]$ gave activities 30–40 times higher than with MAO activation under comparable conditions (7 bar/60–100 °C) (SBI = *rac*-$Me_2Si(Ind)_2$; TIBA = $AlBu^i_3$).[8]

Measurements of propylene polymerisation activities with $(SBI)ZrMe_2$/TIBA/$CPh_3{}^+X^-$ catalysts under conditions free of mass-transport limitations proved to be a very sensitive measure of the anion nucleophilicity (Figure 1).[6] From such data the incremental contribution of the counter anion to the activation energy of the polymerisation process could be calculated. The anion-dependent increase in activity can be due either to an increased number of active sites as the anion becomes less coordinating, or to different transition state energies. The latter implies that the anion must be involved in the rate limiting step. Quenched-flow kinetic studies supported the latter model: with weakly coordinating anions the rate with which each catalytic cycle is completed is enhanced, whereas on the other hand there is no substantial variation in the concentration of active species for different activators, at least for (SBI)Zr-based systems.[9–11] The catalytically active ion pairs in typical low-polarity solvents such as toluene must therefore be regarded as distinct compounds held within the solvent cage, $[Cp^R{}_2M\text{-}R^+ \cdots X^-]$, with no diffusion of free ions.[10,12] It follows from these

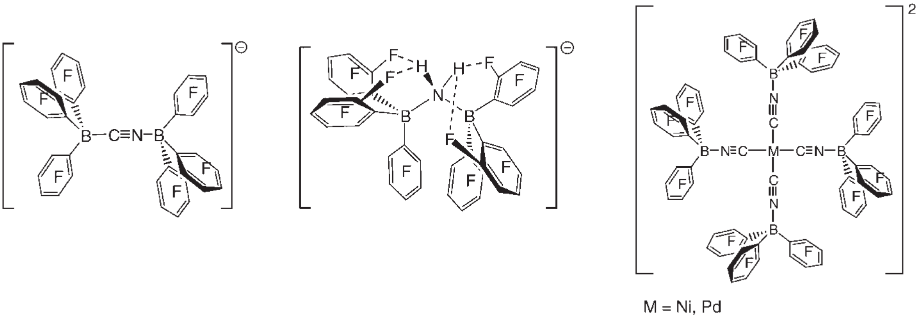

Chart II.

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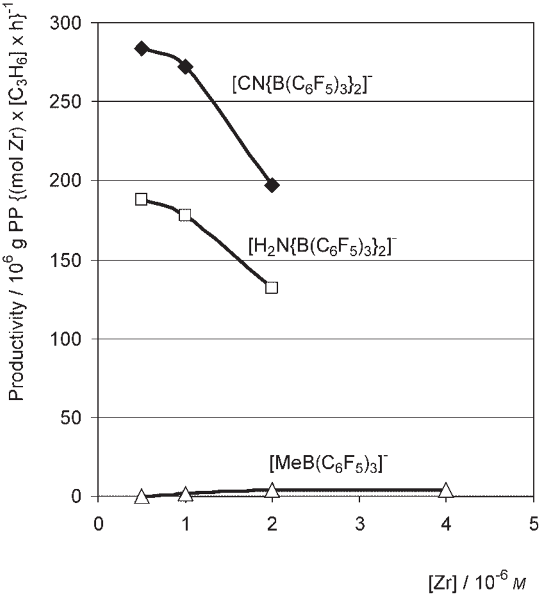


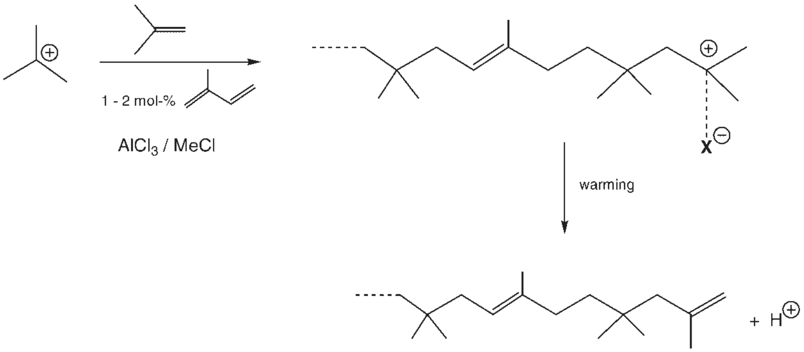
Figure 1.

Anion dependence of propylene polymerisation activities with (SBI)$ZrMe_2$/ TIBA/$CPh_3^{+}X^{-}$ and (SBI)$ZrMe_2$/TIBA/$B(C_6F_5)_3$ catalysts at 25 °C/1 bar propene. Adapted from [6].

considerations that olefin polymerisation proceeds via an associative interchange and not a dissociative mechanism.

Interestingly, the anion effect on the polymerisation rate is not unique to Ziegler-type polymerisations. The copolymerisation of isobutene with isoprene to butyl rubber is the most important example of a carbocationic polymerisation process (Scheme 1).[13–15] It is initiated industrially by an $AlCl_3/H_2O$ slurry in methyl chloride, and in order to suppress chain transfer and achieve sufficiently high molecular weights in the presence of such comparatively basic reactants, the reaction has to be conducted at ca. −100 °C, a highly energy-intensive production method.

Here, too, extremely weakly nucleophilic anions can be applied with advantage: since they possess a much lower proton affinity, chain transfer is reduced, and consequently industrial-standard polymer can be obtained at temperatures as high as −35 °C. Figure 2 shows the temperature dependence of isobutylene copolymerisations as a function of anion structure.[16]



Scheme 1.

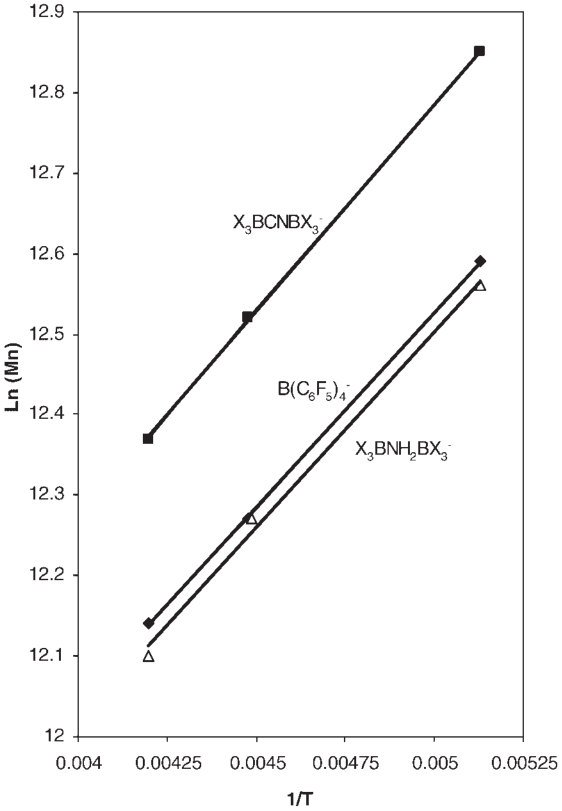


Figure 2.
Dependence of $\overline{M}_n$ on the nature of the counteranion in isobutene/isoprene copolymerisations. The Figure illustrates the similarity of anion dependence to that in propylene polymerisations. Initiator system $[Cp'_2ZrH_2]_2/CPh_3^+X^-$, toluene, 2 mol-% isoprene ($Cp' = C_5H_4SiMe_3$).

Although the polymerisation mechanism and the propagating species in cationic and insertion polymerisations are entirely different, the cationic polymerisation shows exactly the same anion effect as propylene polymerisation, $[CN\{B(C_6F_5)_3\}_2]^- > [H_2N\{B(C_6F_5)_3\}_2]^-] \approx [B(C_6F_5)_4]^-$. In both cases the coordinative tendency of the anion, or its absence, controls the propagation rates.

The tendency of an anion to bind to a Lewis acidic metal centre is reduced if the negative charge is delocalised over as large a volume as possible, but enhanced if a dipole moment is present. In an effort to create even more effective and larger anions, we explored cyanide and cyanamide linkers in combination with $B(C_6F_5)_3$ and Marks' bulky perfluorobiphenylborane $B(C_6F_4\text{-}2\text{-}C_6F_5)_3$ (PBB). PBB reacts with CN^- to give the $[NC\text{-}PBB]^-$ anion; PBB is too bulky to allow the formation of the CN-bridged bis-PBB anion.[17] A frequent side product found in reactions of PBB with nucleophiles is the fluoroborate $[F\text{-}PBB]^-$, previously made by Marks from Ph_3CF and PBB[18] but found here as the product of the rather facile nucleophilic substitution of *ortho*-F atoms in PBB.

Unlike CN^-, the cyanamide anion $N(CN)_2^-$ as a 5-atom linker, overcomes steric hindrance sufficiently and reacts with PBB to give the very large and stable diborate $[N(CN\text{-}PBB)_2]^-$. Its adduct with

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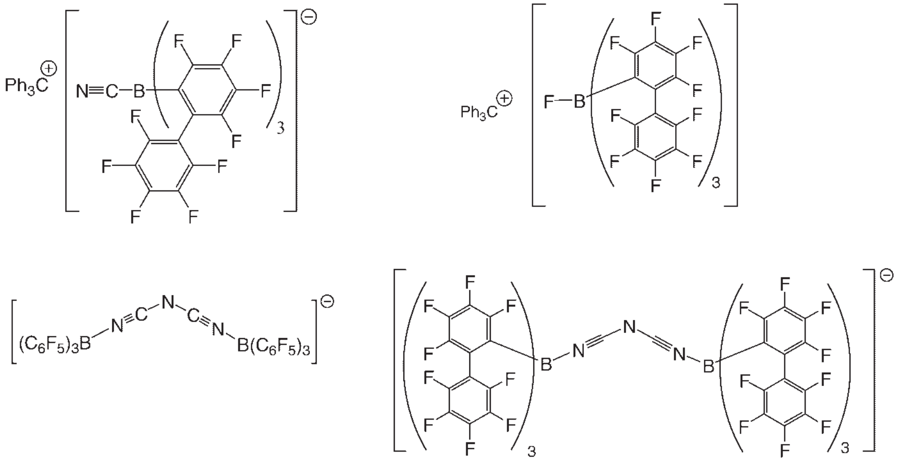

Chart III.

$B(C_6F_5)_3$ is sterically insufficiently protected and unstable. These new anions are illustrated in Chart III.

Using longer linkers and bulky Lewis acidic boranes results in a substantial volume increase. It is useful to compare the sizes of these anions, and of metallocenium cations, by comparing their van der Waals volumes. Figure 3 shows the van der Waals shapes of $[MeB(C_6F_5)_3]^-$ and $[N(CN\text{-}PBB)_2]^-$ in comparison with $[Cp_2ZrMe]^+$. The volume of $[N(CN\text{-}PBB)_2]^-$ is almost four times larger than that of $[MeB(C_6F_5)_3]^-$; and although the

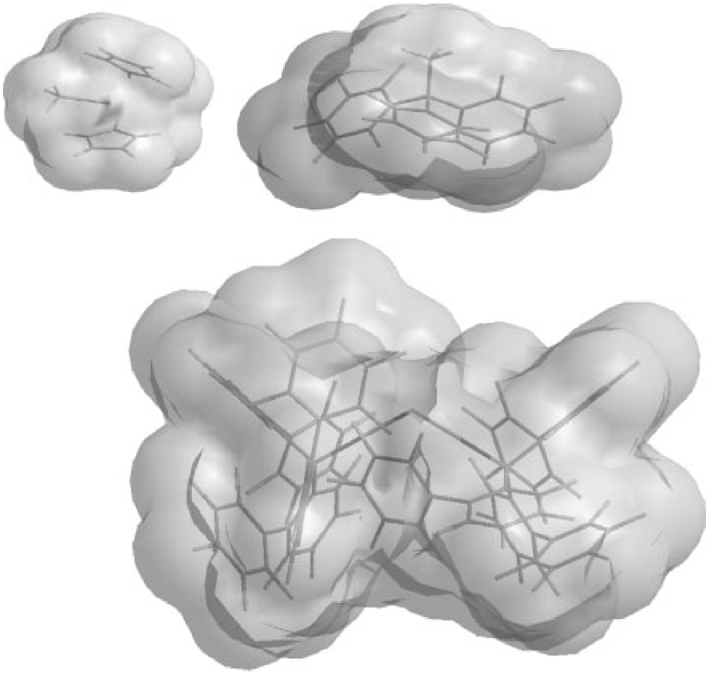

Figure 3.

Van der Waals shapes of $[MeB(C_6F_5)_3]^-$ (top right) and $[N(CNPBB)_2]^-$ (bottom) in comparison with the $[Cp_2ZrMe]^+$ cation (top left). Blue regions indicate negative partial charge.

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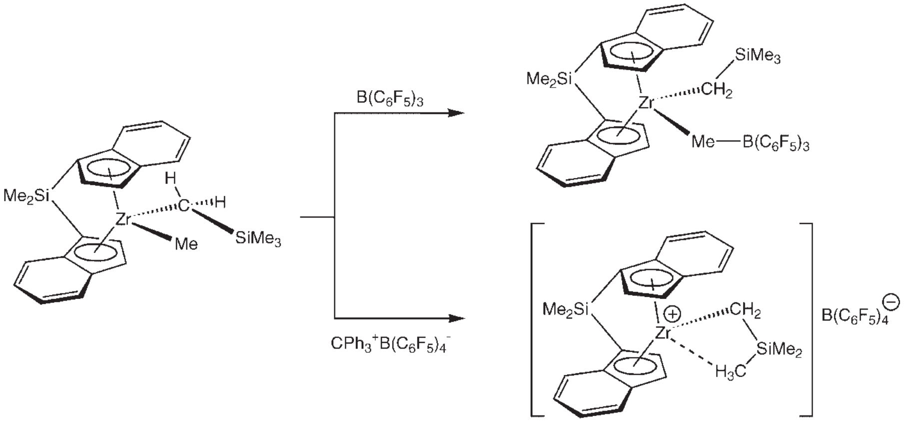
Table 1.
Van der Waals volumes (Å^3) and surface areas (Å^2) of some borate anions and zirconocene cations.

Ion	Surface area / Å^2	Volume / Å^3
$[Cp_2ZrMe]^+$	174	136
$[(SBI)ZrCH_2SiMe_3]^+$	334	313
$[MeB(C_6F_5)_3]^-$	306	277
$[B(C_6F_5)_4]^-$	367	349
$[F\text{-}PBB]^-$	471	503
$[NC\text{-}PBB]^-$	469	510
$[H_2N\{B(C_6F_5)_3\}_2]^-$	512	538
$[N(CNPBB)_2]^-$	728	1013

anion is in principle polar, it is sterically so well shielded that it is capable of forming highly active catalysts, exceeding the performance of the non-polar $[B(C_6F_5)_4]^-$. Table 1 gives the van der Waals volumes and surface areas of a number of metallocenium cations and borate anions.

A particularly useful model for the study of ion pair structure and dynamics proved to be salts of the zirconocene trimethylsilylmethyl cation, $[(SBI)ZrCH_2SiMe_3]^+$.[19] The trimethylsilylmethyl ligand was chosen to mimic a metal-bound polymeryl chain more realistically than is possible with the much-used methyl compounds. The reaction of $(SBI)ZrMe(CH_2SiMe_3)$ with $B(C_6F_5)_3$ or with $CPh_3[B(C_6F_5)_4]$ proceeds with selective methyl abstraction to give the zwitterion $(SBI)Zr(CH_2SiMe_3)(\mu\text{-}Me)B(C_6F_5)_3$ and the ion pair $[(SBI)Zr(CH_2SiMe_3)^+ \cdots B(C_6F_5)_4^-]$, respectively (Scheme 2). The latter proved to be thermally remarkably stable; solutions in toluene or toluene/difluorobenzene show no change at room temperature over a period of several days. These zirconocene derivatives provided useful information about various aspects of metallocene catalysts, notably the stereochemistry and rates of site epimerisation ("chain skipping"), the kinetic differences between propylene and 1-hexene polymerisations,[20] the extent of ion aggregation in catalytically active ion pairs, and the differences in alkyl bonding in inner and outer-sphere complexes (see Scheme 2).[19]

Brintzinger has earlier pointed out the importance of ion aggregation in metallocene-based catalysts both in borate- and MAO-based systems.[21–23] There are significant differences in the structures of these compounds. $(SBI)Zr(CH_2SiMe_3)(\mu\text{-}Me)B(C_{65})_3$ is a tight "inner-sphere" ion pair (ISIP) both in the solid state and in solution and resembles in this respect the methyl derivatives studied by Marks et al.[24–26] $[(SBI)Zr(CH_2SiMe_3)^+ \cdots B(C_6F_5)_4^-]$, on the other hand, behaves as an "outer-sphere" ion pair (OSIP) and has a much higher tendency to aggregate in solution; at $[Zr] = 10$ mM ion hextuples prevail, while at $[Zr] = 2$ mM the compound exists mainly as ion quadruples.[19] Dynamic



Scheme 2.

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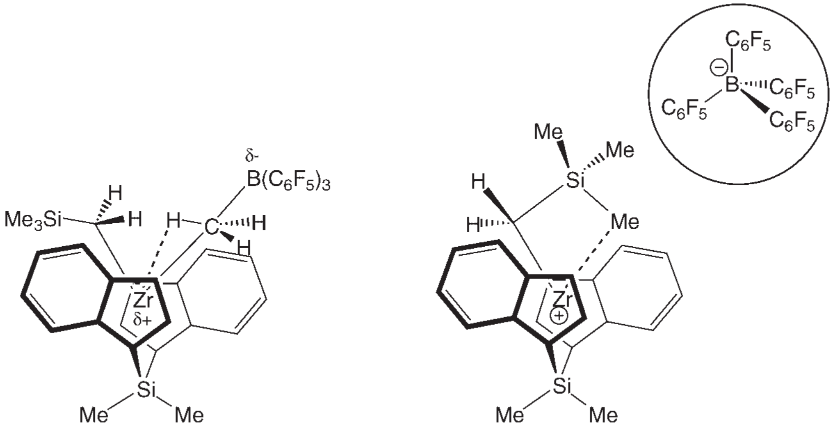
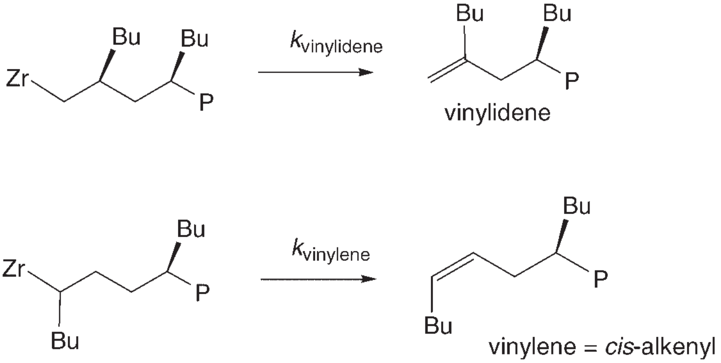


Figure 4.
Alkyl ligand conformation in ISIP (left) and OSIP (right) metallocene catalysts.

processes such as site epimerisation ("chain skipping") are accelerated in such ion aggregates, which might be taken to suggest that such aggregates will also produce faster catalytic chain growth. Although it is possible that at the much lower [Zr] employed under catalytic conditions the quadruples dissociate to simple ion pairs, it has so far not been possible to confirm this assumption. Ion aggregation was also evident from NOE experiments which show interactions between F atoms of the anion not just with the CH_2SiMe_3 ligand but also with the $SiMe_2$ bridge at the "back" of the metallocene. Such interactions are readily explained by the existence of at least ion quadruples.

The difference in anion coordination between $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ compounds is reflected in very different conformations and binding modes of the alkyl ligand. Whereas in $(SBI)Zr(CH_2SiMe_3)(\mu\text{-}Me)B(C_6F_5)_3$ the alkyl ligand points away from the anion, alkyl bonding in $[(SBI)Zr(CH_2SiMe_3)^+ \cdots B(C_6F_5)_4^-]$ involves agostic interactions that can either be described as γ-CH or β-Si-C bonding. In consequence, $B(C_6F_5)_4^-$ is not able to enter the coordination sphere but occupies a rather shallow energy potential minimum at the least hindered side of the open metallocene wedge; models suggest a Zr···B distance of 11–12 Å (Figure 4).



Scheme 3.

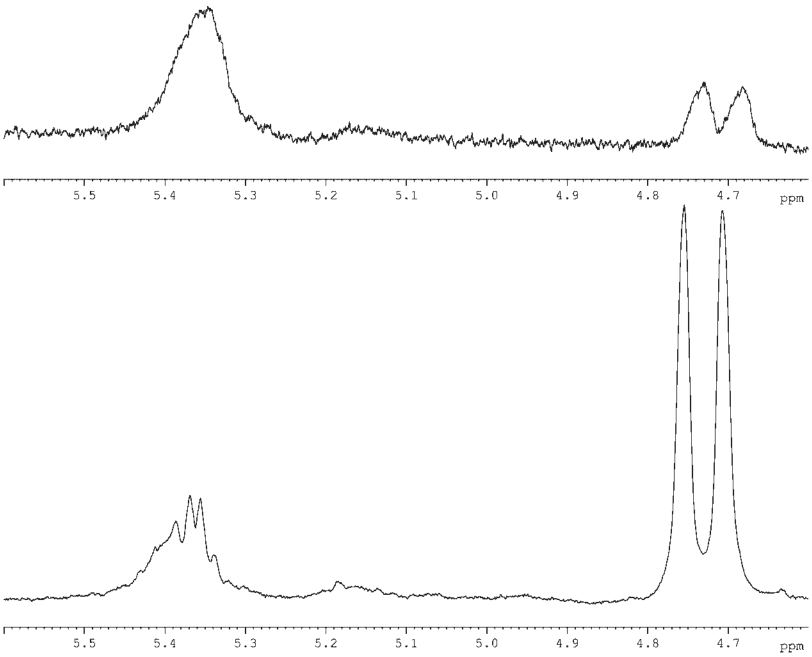


Figure 5.
End-groups of poly(1-hexene) produced with (SBI)Zr(CH_2SiMe_3)(μ-Me)B(C_6F_5)$_3$ at 7.7% conversion / 20 °C (top) and 70% conversion / 40 °C (bottom). Polymerisations conducted in the absence of scavenger (TIBA).

Since these structures must be very similar to catalyst resting states which give rise to chain termination, the possibility of differences in the end group distribution as a function of the ion pair structure naturally suggested itself. This was explored in the case of 1-hexene polymerisations. There are two predominant termination pathways: termination following 1,2-monomer insertion leads to vinylidene end groups, while 2,1-misinsertions gives rise to vinylene structures (Scheme 3). Using the catalyst system (EBI)$ZrMe_2$ / B(C_6F_5)$_3$, Landis et al.[12] established that the formation of vinylene groups is independent of [monomer], while the generation of *cis*-

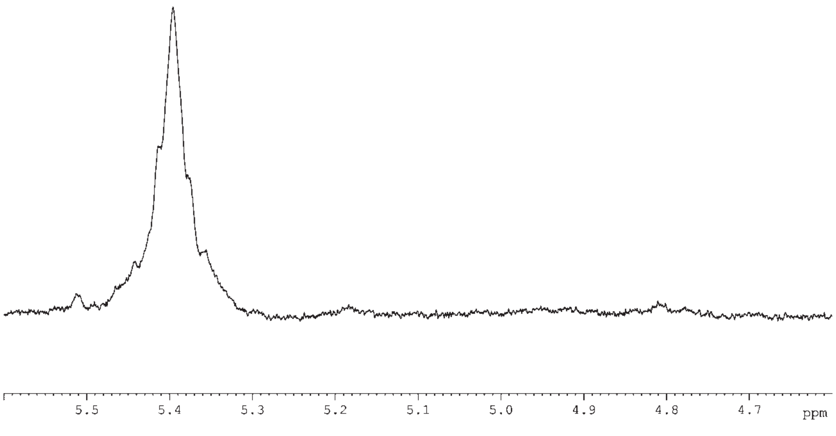


Figure 6.
End-groups of poly(1-hexene) produced with [(SBI)Zr(CH_2SiMe_3)$^+ \cdots$ B(C_6F_5)$_4^-$] at 31% conversion / 20 °C.

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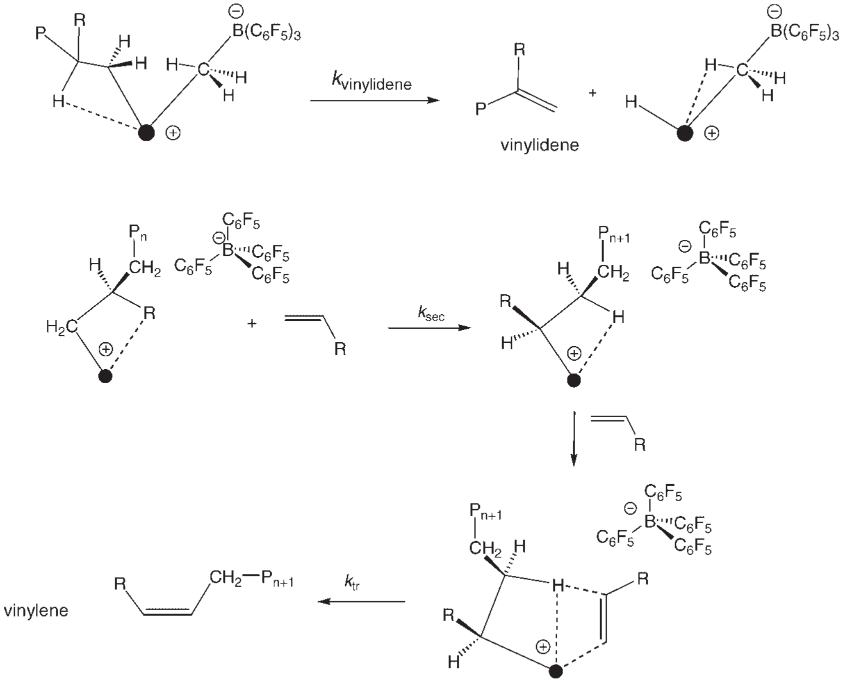

Scheme 4.

alkenyl (vinylene) groups is first-order in [1-hexene] (although with related systems rather variable dependencies for end-group formation have also been reported in the literature[27]). The formation of vinylidene is therefore favoured at low monomer concentrations, or where the structure of the resting state disfavours the approach of monomer.

Figure 5 shows the end groups of poly(1-hexene) produced with (SBI)Zr(CH_2SiMe_3)(μ-Me)B(C_6F_5)$_3$ as catalyst at low

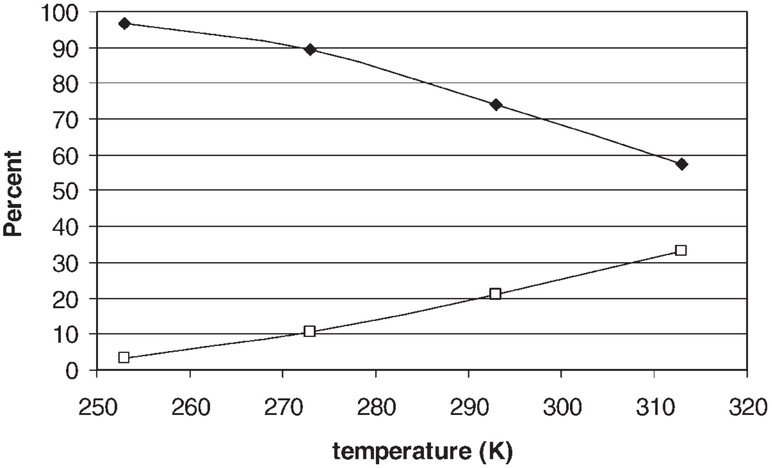

Figure 7.
Temperature dependence of poly(1-hexene) end groups produced with (SBI)Zr(CH_2SiMe_3)(μ-Me)B(C_6F_5)$_3$ catalyst, showing the relative proportions of vinylene (◆) and vinylidene (□)end groups.

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and high conversions. It is evident that a mixture of both vinylene and vinylidene are formed even at high [1-hexene], and that the latter increases significantly as the reaction nears completion. By contrast, as Figure 6 shows, $[(SBI)Zr(CH_2SiMe_3)^+ \cdots B(C_6F_5)_4^-]$ gives only *cis*-alkenyl (vinylene) end groups, independent of the conversion rate. The *cis*-geometry of the alkene was confirmed with J-resolved 2D-NMR spectroscopy. A possible explanation is illustrated in Scheme 4: The strongly coordinating anion $[MeB(C_6F_5)_3]^-$ makes β-H transfer to another monomer more difficult but allows unimolecular reactions, favouring vinylidene. In the $B(C_6F_5)_4^-$ catalyst, on the other hand, the only observed termination is that following a 2,1-misinsertion. Since we did not observe measurable incorporation of these regioerrors into the polymer chain, every misinsertion leads to termination, i.e. $k_{sec} < k_t$, where k_{sec} and k_t, are the rate constants of the 2,1-misinsertion and of chain termination, respectively. It follows that in this regime the rate of 2,1-misinsertion can be determined directly, whereas k_t and the molecularity of the chain termination step remain kinetically inaccessible. However, a transition state involving chain transfer to monomer, as depicted in Scheme 4 for this process, would seem to be sterically more feasible.

The distribution of poly(1-hexene) end groups generated with the $(SBI)Zr(CH_2SiMe_3)(\mu\text{-}Me)B(C_6F_5)_3$ catalyst is temperature-dependent. A series of reactions was conducted at low monomer conversions (<15%) using TIBA as scavenger (Al:Zr = 100). At −20 °C the dominant end group is *cis*-alkenyl (vinylene), with only traces of vinylidene being detectable. The proportion of vinylidene termini increases linearly with the polymerisation temperature (Figure 7). At 20 °C and above, C=C double bond isomerisation to trisubsituted alkenes also takes place, as indicated by a "triplet" at δ 5.17; their proportion rises from 5 mol-% at 20 °C to 8.6 mol-% at 40 °C. These trisubstituted products can arise from both types of end groups. Since such isomerisation products were not evident in polymers produced in the absence of TIBA, it is probable that aluminium alkyls are involved in their formation. The temperature dependence of end group distributions mirrors the findings of Odian et al. for the system *rac*-$Me_2Si(H_4Ind)_2ZrCl_2$ / MAO[27]; in terms of coordinating ability of anions this suggests that $[Me\text{-}MAO]^-$ behaves more like $[MeB(C_6F_5)_3]^-$ than $B(C_6F_5)_4^-$.

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