The (butadiene)metal complex/B(C$_6$F$_5$)$_3$ pathway to homogeneous single component Ziegler–Natta catalyst systems

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The Lewis acid B(C$_6$F$_5$)$_3$ adds to a variety of (butadiene)metal systems to yield zwitterionic complexes that are active homogeneous Ziegler–Natta type olefin polymerization catalysts. The new compounds have been useful in experimental studies gaining information about details of the carbon–carbon coupling reactions at these often fast and selective catalyst systems.

Introduction

There has been significant progress in the development of homogeneous Ziegler–Natta olefin polymerization catalysts in recent years. Early contributions focused mainly on the group 4 derived metal complexes,[1] but recently the use of chelate complexes of late transition metals has further advanced the field.[2] Coordinatively unsaturated alkyl metal cation complexes [L$_n$M–R$^+$] seem to be the initiating as well as the propagating catalytically active species in these very fast and often at the same time very selective olefin polymerization reactions.[3] Usually the catalyst is generated by treatment of a neutral precursor complex, such as *e.g.* L$_n$M(CH$_3$)$_2$ with a suitable activator component. Such reactions with *e.g.* methylalumoxane (MAO), an electrophilic borane, a carbenium ion or a suitable Brønsted acid results in a formal hydrocarbyl anion abstraction [4] with formation of catalytically active [L$_n$MCH$_3$$^+$/anion$^-$] ion pairs,[5] provided that a sufficiently low-nucleophilicity anion was used for or generated in the course of the reaction.[6] Intermolecular ion pairing is an essential but sometimes complicating factor in these systems—with regard to *e.g.* understanding (or even predicting) catalyst activities and selectivities—and it makes mechanistic studies more difficult. Therefore, it was desirable to have a variety of neutral single component analogues of these ubiquitous cationic catalysts available.

Let us assume we could prepare a zwitterionic system (**1**) (see Scheme 1) in which an active cationic metal complex system [L$_n$M$^+$] is connected with a suitable anion component [–X$^-$] by means of a hydrocarbon chain. In its open, zwitterionic form this would probably constitute a reactive single component Ziegler–Natta catalyst system. An incoming α-olefin would

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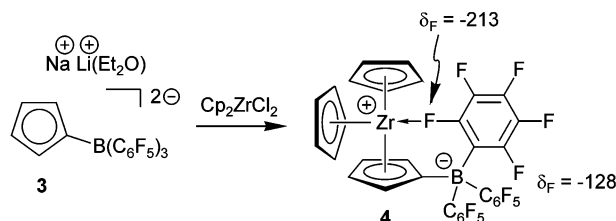
Scheme 1

coordinate to the metal center and then subsequently insert into the metal–carbon bond. Repetition of this process would bring the metal cation and anion parts of such a betaine system apart from each other, until a chain transfer would eventually lead the system into the usual olefin polymerization cycle of the active Ziegler–Natta catalysts. In the absence of an alkene, internal ion pair formation (**2**) would probably protect the active catalyst in an equilibrium situation.

Practical realization of this concept required a search for both the right type of the anion component and suitable precursors for a simple synthesis of such zwitterionic systems.[7] In this account we will describe our approach to such single component Ziegler–Natta catalysts that was based on the chemistry of η^4-butadiene metal complexes.[8]

Search for suitable anion components

What is the right anionic building block [–X$^-$] for such zwitterionic catalysts? It must be able to protect its [L$_n$M$^+$] cation unit by internal coordination, but at the same time kinetically allow for a rapid opening of the cyclic structure **2** to its catalytically active betaine isomer **1** (see Scheme 1). From suitable model systems it became clear that internal alkyl borate/metal interactions[5,9] and internal C–F/metal contacts were good candidates for our purpose.[10] The latter will be illustrated using two selected examples.

The (C$_6$F$_5$)$_3$B-substituted cyclopentadienide reagent **3** reacts with Cp$_2$ZrCl$_2$ to yield the zwitterionic tris(cyclopentadienyl) zirconium complex **4** (see Scheme 2).[11] All three Cp-type
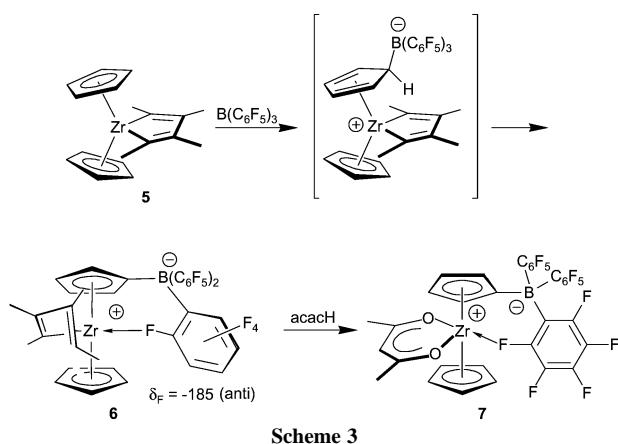

Scheme 2

ligands in **4** are η^5-coordinated. The [Cp$_3$Zr$^+$] cation behaves as a 16-electron system, since it contains an electron pair located in a ligand centered molecular orbital.[12] Consequently, one *ortho*

fluorine atom from a B–C_6F_5 group in **4** coordinates to the metal center to complement its coordination sphere.[13] This has become evident from the X-ray crystal structure analysis of **4** [d(Zr–F) = 2.310(3) Å, angle Zr–F–C: 138.0(3)°],[14] and the divalent fluorine atom in **4** gives rise to a characteristic ^{19}F NMR resonance at $\delta = -213$, shifted upfield by >80 ppm relative to a typical *o*-F resonance of the C_6F_5 ring ($\delta^{19}F = -128$ in **4**). Complex **4** exhibits dynamic ^{19}F NMR spectra. From the coalescence of the *ortho*-F(C_{Ar}) signals a Gibbs activation energy of $\Delta G^{\neq}_{(Zr-F)diss}(253\ K) = 10.2 \pm 0.2$ kcal mol^{-1} was obtained.[15] This value is probably close to the Zr–F(C_{Ar}) bond dissociation energy in **4** and in a good energetic range for a dynamic active catalyst site protection.

A similar structural situation was encountered when the metallacyclopentadiene **5** (see Scheme 3) was treated with
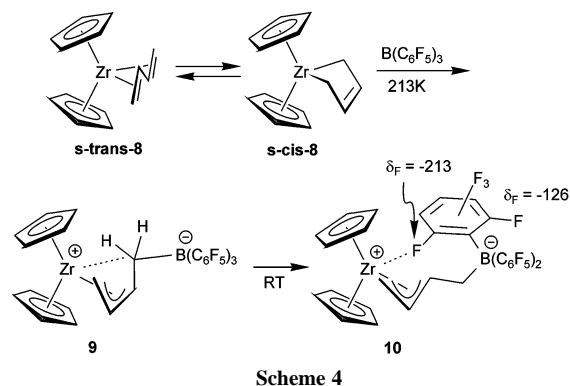

Scheme 3

B(C_6F_5)$_3$. Electrophilic addition at a Cp-ring occurred, followed by internal proton transfer to yield **6** (two diastereoisomers).[16] The product (**6**) again contains a pronounced Zr–F(C_{Ar}) interaction, equal in strength to **4** [**6**: d(Zr–F): 2.322(2) Å]. The zirconium/F(C_{Ar}) interaction in this type of complex appears structurally robust: cleavage of the σ-ligand by treatment of **6** with *e.g.* acacH cleanly furnished the corresponding zwitterionic zirconocene(acac) complex **7** with preservation of a Zr···F(C_{Ar}) contact [**7**: d(Zr–F) = 2.42(2) Å].

The addition of B(C_6F_5)$_3$ to (butadiene)metallocenes and related compounds

In view of the reaction depicted in Scheme 3 there might be a selectivity problem when B(C_6F_5)$_3$[17] is reacted with (butadiene)zirconocene.[18,19] The electrophile could in principle add either to the 'odd-closed' (here: Cp) or the 'even-open' π-ligand (here: butadiene). It is well known that electronic control governs a similar selectivity situation in the addition of nucleophiles to the π-ligands of a variety of cationic metal complexes (the 'Davies–Green–Mingos rules').[20] It seems that electrophilic attack to (conjugated diene)metallocenes and related complexes are governed by similar principles. The experiment shows that B(C_6F_5)$_3$ apparently catalyzes the (s-*trans*-/s-*cis*-η⁴-butadiene)ZrCp$_2$ equilibration effectively at low temperature and adds selectively to a terminal CH_2– group of the diene ligand. At 213 K we observe the selective formation of the *cisoid* zwitterion **9**, that rearranges to the *transoid* isomer **10** upon warming (Scheme 4).[8]

The analogous reaction takes place with a great variety of (butadiene) group 4 metallocenes including many non-bridged as well as *ansa*-metallocenes that have been applied for generating active homogeneous Ziegler–Natta catalysts.[1,21] Fig. 1 shows a view of the parent compound **10**, featuring the strongly distorted (π-allyl)Zr unit[22] (Zr–C1: 2.339 Å, Zr–C2: 2.494 Å, Zr–C3: 2.528 Å) and the pronounced Zr–F(C_{Ar}) interaction (Zr–F: 2.423 Å, Zr–F–C_{Ar}: 140.0°).
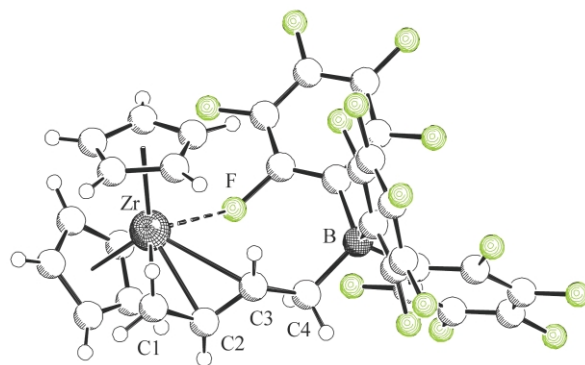

Scheme 4

Fig. 1 A projection of the molecular structure of the zwitterionic zirconocene–borate complex **10**.

The Zr–F(C_{Ar}) interaction of **10** remains present in solution (^{19}F NMR: $\delta = -213$). Dynamic ^{19}F NMR spectroscopy revealed that this Zr–F interaction is (reversibly) broken and the *ortho* fluorine atoms interchanged with an activation energy of $\Delta G^{\neq}_{(Zr-F)diss}(233K) = 8.1 \pm 0.3$ kcal mol^{-1} (in d$_8$-toluene). In this non-coordinating solvent the π-allyl moiety of **10** shows a very slow dynamic behavior $(\Delta G)^{\neq}_{enant}(350\ K) \approx 17$ kcal mol^{-1}. However, in d$_8$-THF the allyl inversion process becomes very rapid $(\Delta G^{\neq}\ (207\ K) \approx 10$ kcal mol$^{-1})$. The Zr–F(C_{Ar}) bond is cleaved upon the addition of suitable donor ligands (CO, PMe$_3$). Both a CO adduct (Cp$_2$Hf)[8] and a PMe$_3$[23] adduct were characterized by X-ray diffraction. These compounds may potentially serve as close models of η²-alkene coordination products in the initial stages of the Ziegler–Natta cycles originating from such metallocene–borate–betaine systems (see below). Fig. 2 shows a view of the zwitterionic
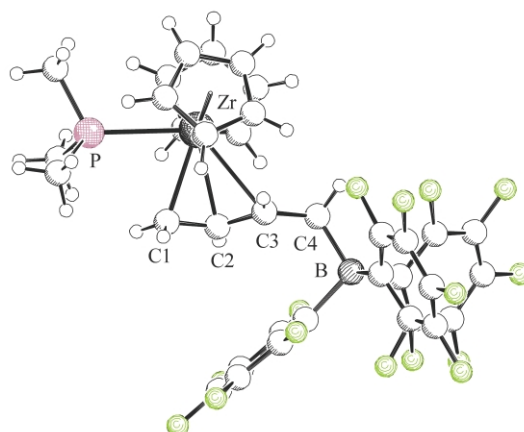

Fig. 2 A view of the phosphane adduct (**11**) derived from **10** by treatment with PMe$_3$.

complex (**11**) formed by treatment of **10** with PMe$_3$. The π-allyl unit in **11** is again distorted (Zr–C1: 2.443(5) Å, Zr–C2: 2.526(4) Å, Zr–C3: 2.681(4) Å, Zr–P: 2.705(1) Å).

The zwitterionic structure opens up even further when steric bulk is introduced. Treatment of (butadiene)bis(pentamethylcyclopentadienyl)zirconium with $B(C_6F_5)_3$ leads to the formation of the zwitterionic complex **12** (see Fig. 3), that has the borate
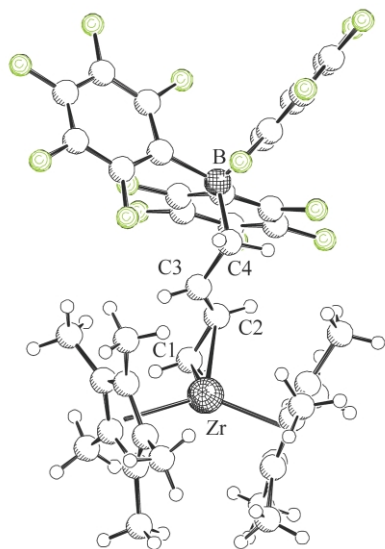

Fig. 3 Molecular structure of $Cp^*_2Zr(C_4H_6)B(C_6F_5)_3$ (**12**).

anion moiety oriented away from the $[Cp^*_2Zr^+]$ cation unit.[24] The polar end groups seem to be connected by a σ,π-allyl-CH_2-bridge (Zr–C1: 2.337(4) Å, Zr–C2: 2.488(4) Å, Zr–C3: 2.722(4) Å).

We have found examples where the rearrangement of the primary addition product (*e.g.* **9** in Scheme 4) was not observed. In the case of some specific backbones the corresponding *cisoid* betaines could even be characterized by X-ray diffraction.[21] Complex **13** (see Fig. 4) is a typical example. Its formation from
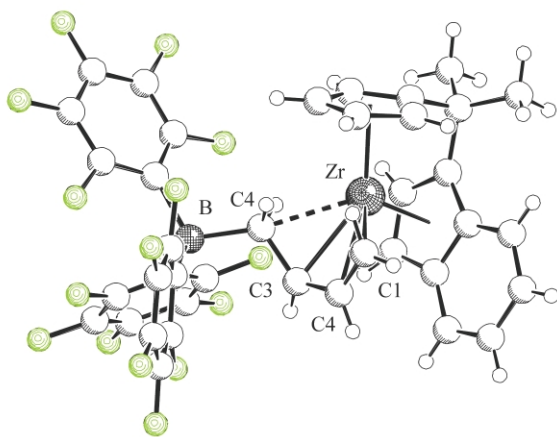

Fig. 4 Molecular geometry of **13**.

the respective (η^4-butadiene)metallocene complex is in so far remarkable as only one out of the four possible *cisoid* zwitterions was selectively formed. In **13** there seems to be a pronounced internal alkyl/zirconium electrostatic ion pair interaction[5,25] (Zr···C4: 2.498(2) Å) that contributes considerably in the bonding of the σ,π-allyl-type C_4H_6–$B(C_6F_5)_3$ ligand to zirconium (Zr–C1: 2.333(3) Å, Zr–C2: 2.521(2) Å, Zr–C3: 2.508(2) Å).

The dimethylsilanediyl-bridged Cp/amido group 4 metal complexes, the 'constrained geometry' catalyst precursors,[26,27] show a similar chemistry. Reaction of the (s-*cis*-η^4-butadiene)Zr(Cp*SiMe$_2$NR) system **14**[28] with $B(C_6F_5)_3$ yields a 65:35 mixture of the 'supine' and 'prone'[29] zwitterion isomers **15A** and **15B** (see Scheme 5). The activation barrier of the **15A** ⇌ **15B** interconversion (in toluene-d_8) was determined as $\Delta G^{\neq}_{diast}(303\,K) = 17.6 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$. Cowley, Jones *et al.*
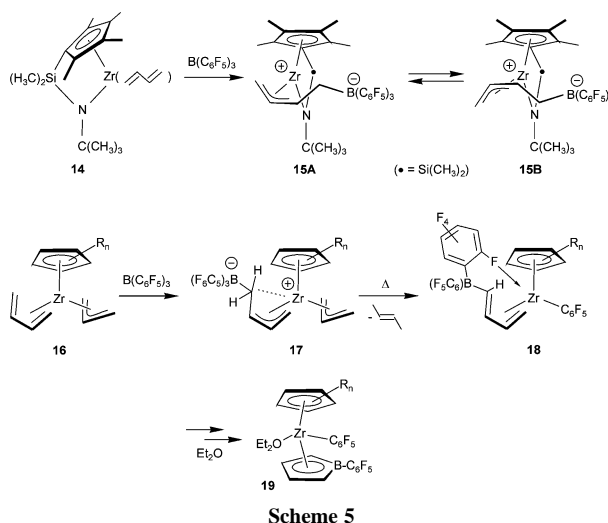
Scheme 5

characterized a corresponding titanium example by X-ray diffraction and even described an analogous $(Cp^*SiMe_2NR)Ti$ $[\eta^3\text{-}C_4H_6\text{-}Al(C_6F_5)_3]$ complex.[30,31] Bochmann *et al.* have shown that $B(C_6F_5)_3$ adds cleanly to the 'even-open' butadiene ligand in (η^5-Cp^R)(η^3-allyl)(η^4-butadiene)Zr (**16**)[32] to initially yield the *cisoid* adduct **17** (see Scheme 5). In this case a subsequent series of thermally induced reactions resulted in C_6F_5 transfer, concomitant with borylation of the butadiene ligand (**18**), and ultimately in the formation of a borole ligand to yield (**19**).[33]

The hetarene-modified boron Lewis acid (*N*-pyrrolyl)$B(C_6F_5)_2$ adds to (butadiene)zirconocene in the same way to yield the transoid $Cp_2Zr[\eta^3\text{-}C_3H_4\text{-}CH_2B(C_6F_5)_2\ (\text{pyrrolyl})]$ zwitterion **20**. Here, a rather strong internal pyrrolyl (C_α)–Zr contact ($\Delta G^{\neq}_{diss}(223\,K) = 15.0 \pm 0.3\ \mathrm{kcal\ mol^{-1}}$) prevails over a weaker possible Zr–$F(C_{Ar})$ interaction (see Fig. 5). The
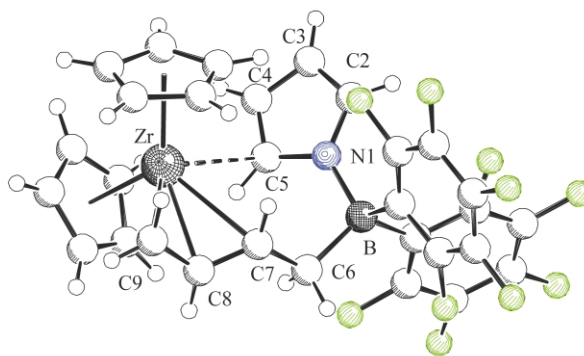

Fig. 5 Molecular structure of the (butadiene)$ZrCp_2$/(*N*-pyrrolyl)-$B(C_6F_5)_2$ derived zwitterionic addition product **20**.

stronger internal pyrrol–metal coordination makes **20** a much less active Ziegler–Natta catalyst as compared to its $B(C_6F_5)_3$ derived analogues.[34]

Catalytic features and mechanistic studies

A great many of the metallocene(butadiene)borate zwitterions (and related systems) were found to be catalytically active in α-olefin polymerization. The isolated or *in situ* prepared homogeneous Ziegler–Natta catalyst systems on the (butadiene)metallocene/$B(C_6F_5)_3$ basis usually exhibited similar activities and stereoselectivities as the analogous homogeneous olefin polymerization catalysts generated by a variety of other common activation methods, especially the metallocene dichloride/methyl alumoxane procedure. The parent (butadiene)zirconocene/$B(C_6F_5)_3$ system polymerized propene to yield atactic polypropylene.[8]

1-Alkene insertion into **10** commenced at *ca.* −35 °C in d8-toluene solution, as monitored directly by NMR spectroscopy. Initially, a selective single alkene insertion reaction was monitored, leading to the formation of **21**. Within a small temperature window up to *ca.* 0 °C this intermediate appears to be protected from further 1-alkene insertion by a weak intramolecular π-coordination and an internal ion pair interaction (see Scheme 6). Above *ca.* 0 °C complex **21** is rapidly


Scheme 6
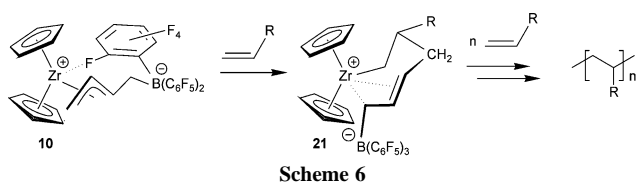
consumed in the presence of *e.g.* ethene to give polyethylene.[35]

The zwitterionic catalyst system **22**, generated from *rac*-(η4-butadiene)(dimethylsilanediyl-bis-1-indenyl)zirconium and B(C6F5)3, produces isotactic polypropylene at +40 °C in toluene solution (with some triisobutylaluminium added as a moisture scavenger) with a catalyst activity of $a \approx 800$ kg[PP] mol[Zr]$^{-1}$·h^{-1}·bar(propene)$^{-1}$. The ^{13}C NMR methyl pentade analysis of the obtained polymer showed a >90% mmmm methyl pentade intensity and indicated a stereocontrolled CC-coupling process by enantiomorphic site control. At −15 °C the stoichiometric single propene insertion process was observed giving rise to the formation of only two diastereoisomeric mono-insertion products in a close to equimolar ratio. Opening of the organometallic ring structure by the addition of d8-thf gave two final propene mono-insertion products **23A** and **23B** in the same 60:40 ratio (see Scheme 7).[36]


Scheme 7
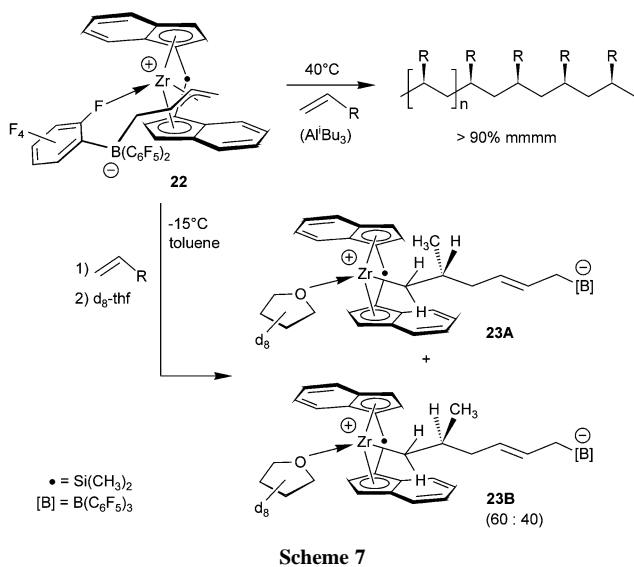
This means that the very first insertion of the prochiral α-olefin into the Zr–C bond of the chiral metallocene catalyst proceeds almost completely stereo-unselectively, whereas all subsequent CC-bond formations take place with a high stereoselectivity. These and a number of similar results from other research groups indicate that the stereocontrol at such catalysts is not taking place directly between the chiral metallocene backbone and the incoming prochiral alkene, but by involvement of the growing σ-ligand chain.[1,37,38] It is likely that a stereochemical relay mechanism is operative, in which an agostic M–H–C interaction at C$_\alpha$ of the σ-chain provides an auxiliary carbon chirality center that effectively controls the chain-growth stereochemistry (see Scheme 8).[39,40] In this scheme the growing polymer chain at the α-carbon atom plays a decisive role for stereocontrol,[41] favoring an arrangement of

Scheme 8
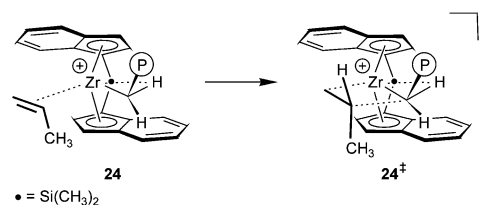
the next 1-alkene that is governed by avoiding unfavorable steric interaction between the respective bulky substituents. The controlling auxiliary carbon center is consumed in every single olefin addition/CC-coupling sequence, and an analogous controlling stereogenic C-center α-positioned to the metal is newly constructed in each of these steps, with its relative stereochemistry itself being controlled by the chiral metallocene backbone.

It is likely that the actual stereocontrol takes place at the insertion transition state (**24**$^{\neq}$) rather than at the stage of its preceding (π-alkene) alkyl metallocene cation intermediate (**24**). There is evidence that rate (and selectivity) determining alkene insertion is preceded by a rapid olefin coordination/dissociation equilibrium step at many homogeneous Ziegler–Natta catalyst systems. Some of this evidence comes from an experimental characterization of the alkene addition/insertion reaction profile of a series of bent metallocene and 'constrained geometry' catalysts using their respective butadiene/B(C6F5)3 zwitterion systems (see Fig. 6).[42,43] By a combination of a
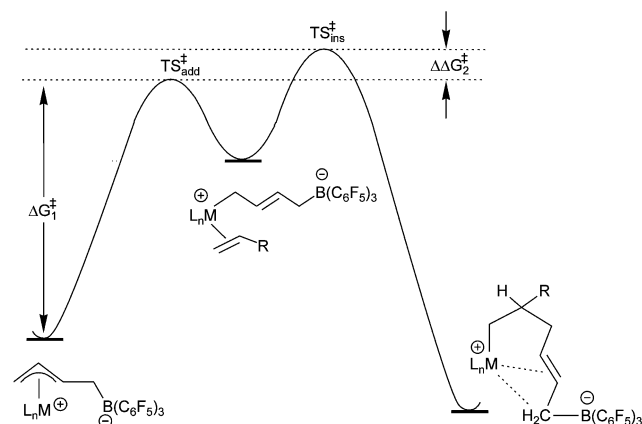

Fig. 6 Alkene coordination/alkene insertion energy profile as it was determined with the aid of the zwitterionic L$_n$M[C4H6B(C6F5)3] catalyst systems.

dynamic NMR study and a kinetic study of the primary 1-alkene insertion (leading to **21** or its analogues) we were able to locate the two essential transition states of olefin addition (TS$^{\neq}_{add}$) and olefin insertion (TS$^{\neq}_{ins}$) by determining $\Delta G^{\neq}_1$ and $\Delta\Delta G^{\neq}_2$. For the systems investigated the olefin adds and dissociates between a few times up to more than a hundred times, depending on the specific catalyst framework, before eventually insertion and CC-coupling actually occurs.[42] It appears that close interaction of groups and substituents in the actual insertion transition state represents the decisive influence on the specific catalyst behavior.

Above *ca.* 0 °C the mono-olefin insertion products (*e.g.* **21**) react further with added 1-alkenes by multiple sequential insertion. After each insertion step there is a possible competition between chain transfer and further chain growth. In this respect this stoichiometric initiation phase probably may be regarded as a very close model of the actual repetitive olefin polymerization cycle, only that at its end a charged [hydrocarbyl–B(C6F5)3$^-$] borate anion is liberated. The formation of such oligomeric [R–B(C6F5)3$^-$] anion distributions was monitored by electrospray mass spectrometry (ESI–MS) obtained after a direct injection of samples from the reaction mixture. For

a representative example originating from propene insertion at the zwitterionic $(MeCp)_2Zr(butadiene)/B(C_6F_5)_3$ catalyst see Fig. 7.[44]
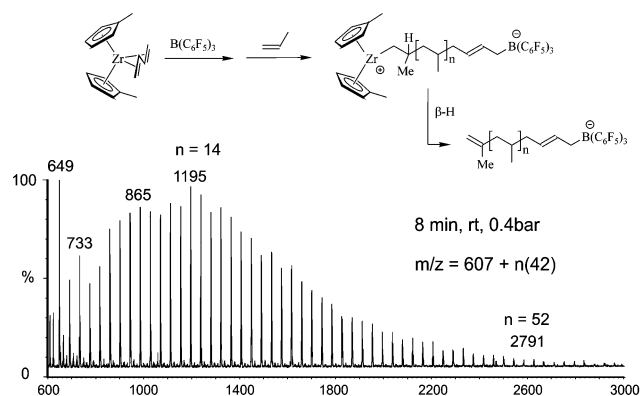
Fig. 7 ESI–MS of an oligomeric $[R–B(C_6F_5)_3{}^-]$ mixture obtained at the $(MeCp)_2Zr(butadiene)/B(C_6F_5)_3$ catalyst (8 min, r.t., 0.4 bar propene).

A close inspection of the ESI–MS spectrum depicted in Fig. 7 reveals that only a singular type of oligomeric anion is formed at the zirconocene$[C_4H_6–B(C_6F_5)_3]$ catalyst (**10A**); the expected isotope pattern was observed for each signal (see Fig. 8).
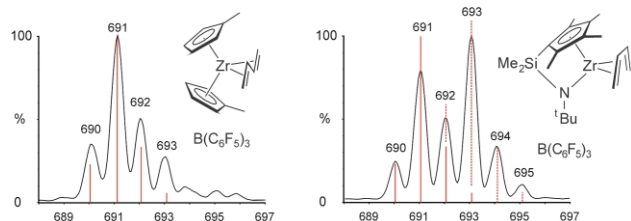
Fig. 8 Representative measured and calculated ESI–MS $[R–B(C_6F_5)_3{}^-]$ features obtained at two homogeneous metal(butadiene)/$B(C_6F_5)_3$ catalysts.

A different oligomeric $[R–B(C_6F_5)_3{}^-]$ anion pattern was obtained from the $(Cp*SiMe_2NtBu)Zr[C_4H_6–B(C_6F_5)_3]$ catalyst. Here we observed that the expected $m/z = 607 + n(42)$ oligomeric $[X^-]$ series is accompanied by an additional $[(X + 2)^-]$ series of almost equal intensity (see Fig. 8). This may potentially originate from a CH activation process that involves attack of the active chain end at the 'constrained geometry' catalyst framework (see Scheme 9). Our model study may have
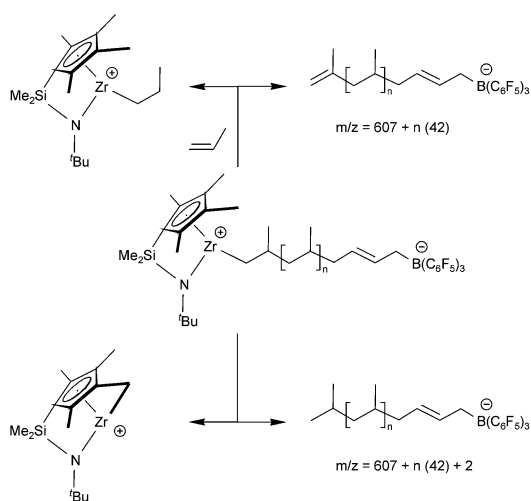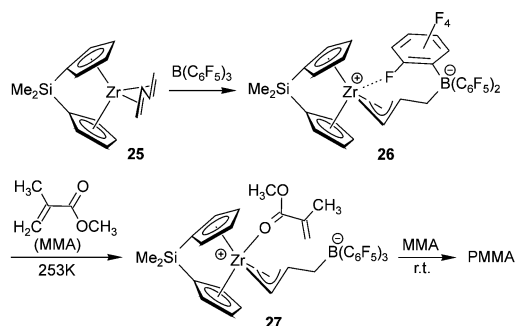

Scheme 9

revealed the presence of a second competing alkene polymerization pathway at this important type of homogeneous Ziegler–

Natta catalyst, although this needs to be confirmed by isotopic labelling.

Addition and insertion of a functionalized olefin

The controlled coordinative polymerization of functionalized olefins has remained a great challenge. Early work by Brookhart *et al.* has shown that *e.g.* ethene/methyl methacrylate diblock copolymers can be formed at some late metal Ziegler-type catalysts.[45] Collins and Soga[46] have demonstrated that poly-(methyl methacrylate) can be obtained by means of a group transfer-type process at dual site group 4 bent metallocene systems [*e.g.* $Cp_2ZrCH_3{}^+$/$Cp_2Zr(CH_3)_2$; the polymer obtained at this system is mostly syndiotactic PMMA]. Eventually, the groups of Gibson[47] and Höcker[48] have shown that a number of alkylidene-bridged dialkyl zirconocene systems, when activated by treatment with $B(C_6F_5)_3$ or $[HNR_3{}^+][BAr_4{}^-]$, produced PMMA. When suitably substituted *ansa*-metallocenes were employed, this led to the formation of isotactic poly-(methyl methacrylate), which was taken as a strong indication for a polymerization mechanism taking place in the coordination sphere of a single active metal center.[49]

We have used a variety of *ansa*-zirconocene(butadiene)/$B(C_6F_5)_3$ systems to obtain further information about the possible pathways followed in methyl methacrylate carbon–carbon coupling at such catalysts. Several variants and examples were employed. Treatment of the dimethylsilandiyl-bridged *ansa*-zirconocene(butadiene) complex **25**[19] with $B(C_6F_5)_3$ furnished the metallocene-borate betaine system **26** (Scheme 10).[21] It was shown by a X-ray single crystal structure
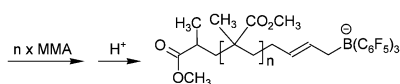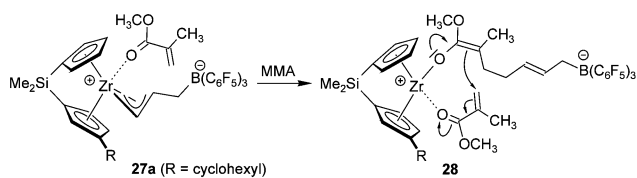

Scheme 10

analysis and by NMR investigation that the dipolar complex contains a distorted *syn*-substituted η^3-allyl unit and features a typical *ortho*-$F(C_{Ar})$ coordination to the early transition metal.[21]

The dipolar complex **26** reacts cleanly with methyl methacrylate at low temperature. The ^1H NMR spectrum of the reaction mixture in d_8-toluene at 253 K shows that the $Zr\cdots F(C_{Ar})$ linkage was cleaved and that a single methyl methacrylate monomer was added to the electrophilic zirconium center. A typical ^1H NMR spectrum (see Fig. 9) shows the signals of free MMA in addition to the resonances of coordinated MMA of the resulting 1:1 addition product. Typically, the $=CH_2$ ^1H NMR resonances are shifted from δ 6.01 and 5.07 (free MMA) to δ 5.29 and 5.04. Most characteristic is the typical shifting of the ^{13}C NMR ester carbonyl resonance by *ca.* 10 ppm from δ 168.2 (free MMA) to δ 178.4 upon complexation of this polar monomer to the cationic zirconocene subunit in **26**.[50]

Raising the temperature eventually results in the consumption of the added free polar monomer with formation of poly(methyl methacrylate). The negative ion ESI-MS spectra obtained from representative samples from such reaction mixtures after quenching have revealed the formation of a series of oligomeric anions that contained the $[–C_4H_6–B(C_6F_5)_3{}^-]$ terminus and was probably formed by means of a sequential incorporation of methyl methacrylate monomers into the zirconium–carbon bond as schematically depicted in Scheme
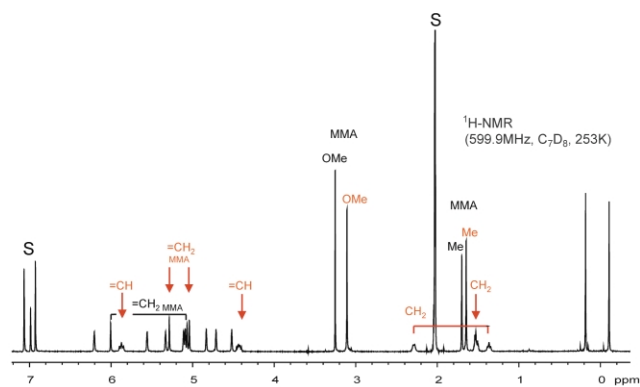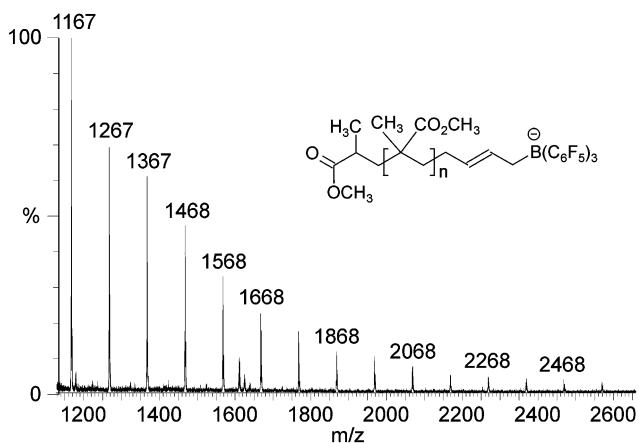
Fig. 9 ^{1}H NMR spectrum of the 1:1 adduct **27** of methyl methacrylate and **26** (600 MHz, d$_8$-toluene, 253 K). Black: free MMA. Red: coordinated MMA and [CH$_2$CHCHCH$_2$B(C$_6$F$_5$)$_3$$^-$].

11, starting from the adduct **27**. The specific example of the oligomeric distribution shown in Fig. 10 was derived from a specifically substituted *ansa*-metallocene system (**26a**, R = cyclohexyl).[51]
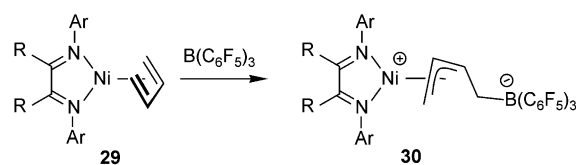

Scheme 11

Fig. 10 Negative ion ESI-MS of the [H-(PMMA)–C$_4$H$_6$–B(C$_6$F$_5$)$_3$$^-$] product distribution obtained from the reaction of excess methyl methacrylate with the catalyst system **27a**.

Late transition metal systems

Homogeneous Ziegler–Natta catalysts based on chelate ligand complexes of transition metals from the right side of the periodic table have become of great interest in recent years.[2] We have, therefore, investigated whether zwitterionic metal(butadiene)/B(C$_6$F$_5$)$_3$ complexes were also formed at late transition metal systems. Mixed 'diazadiene'-butadiene complexes of nickel have been known for many years. We have now treated examples of the chelate Schiff-base (η^4-s-*cis*-butadiene)Ni complexes **29**[52] with B(C$_6$F$_5$)$_3$. A clean and selective addition to the butadiene terminus is observed to yield the zwitterionic L$_n$Ni[η^3-C$_3$H$_4$–CH$_2$B(C$_6$F$_5$)$_3$] complex **30** (see Scheme 12).[53] The X-ray crystal structure analysis (see Fig. 11) has revealed that a *cisoid* η^3-allyl-type coordination is present (Ni–C1 =

Scheme 12
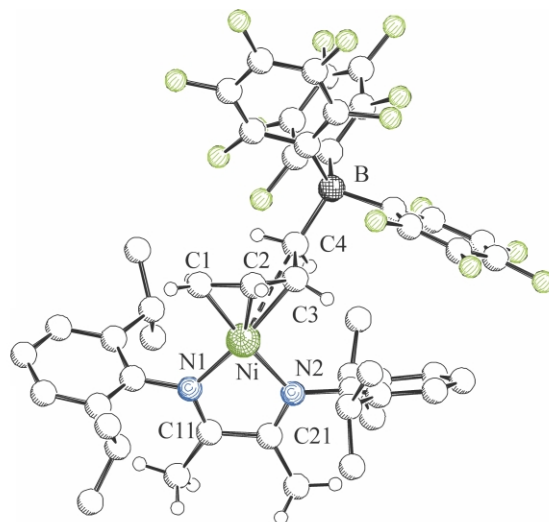
Fig. 11 Molecular structure of **30**.

2.007(2) Å, Ni–C2 = 1.968(2) Å, Ni–C3 = 2.048(2) Å). There seems to be a weak residual internal ion pair interaction between the late transition metal and the CH$_2$-[B] moiety (Ni⋯C4: 2.803(2) Å). At 80 °C a rearrangement to the transoid π-allyl-type betaine isomer takes place.[54]

The zwitterionic complexes show reasonable catalytic ethene polymerization activities in the presence of Al(iBu)$_3$. Polyethylene with a characteristically methyl-branched structure[55] was obtained using these chelate (Schiff-base ligand)Ni/butadiene/B(C$_6$F$_5$)$_3$-betaine catalyst systems at ambient temperature. The presence of excess of tri(isobutyl)aluminium seems to be necessary to obtain a reasonable polymerization activity. Therefore, it needs to be resolved whether some additional activation process is taking place in such reaction mixtures or if the complexes **30** induce the polymerization reaction in a similar way as shown with the respective metallocene systems. In the latter case, studying the system **30** could contribute to the ongoing discussion about the formation of the active catalyst species from homogeneous Ziegler–Natta catalyst precursors that lack the necessary metal–carbon σ-bond at an initial stage of the activation process.[56–58]

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