

The (butadiene)zirconocene route to active homogeneous olefin polymerization catalysts

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Abstract

(Butadiene)zirconocene is observed to exist as an equilibrium mixture of (*s-cis*-) and (*s-trans*- η^4 -C₄H₆)ZrCl₂ isomers. The system adds a variety of unsaturated organic reagents to form metallacyclic (allyl)metallocene products. In some cases, a second equivalent of a reagent is taken up, which forms the basis of a variety of useful template coupling reactions of butadiene at the bent metallocene framework. The Lewis acid B(C₆F₅)₃ adds to (butadiene)zirconocene and to a great variety of butadiene complexes of *ansa*-metallocenes and related systems to give zwitterionic metallocene–butadiene–borate betaines. Most of these systems are active homogeneous Ziegler–Natta olefin polymerization catalysts, that do not require additional activation. Catalyst activities are often in a similar range to those observed for other catalyst activation procedures used in this chemistry. In the case of the (butadiene)metallocene/B(C₆F₅)₃ systems, we can often observe the first olefin insertion step. This feature was utilized to carry out a variety of mechanistic studies of the essential carbon–carbon coupling steps that take place at such bent metallocene catalyst systems. Even reactions with the functionalized monomer methylmetacrylate could be followed in this way. Some chelate ligand late metal systems were also included in these studies. However, these systems mostly behaved differently even in cases where some structural similarities were observed.

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Keywords: (Butadiene)zirconocene; Template reactions; Metallocene catalysts; Ziegler–Natta catalysis; Olefin polymerization

1. Introduction

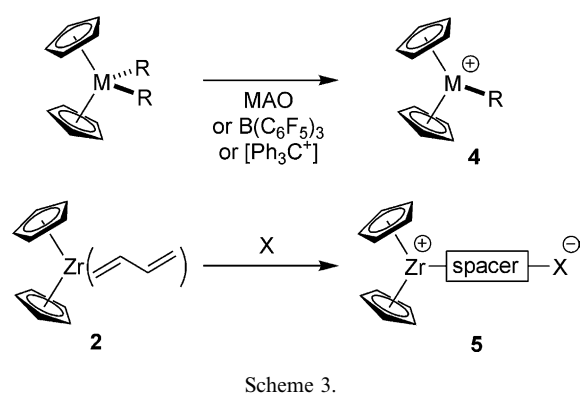
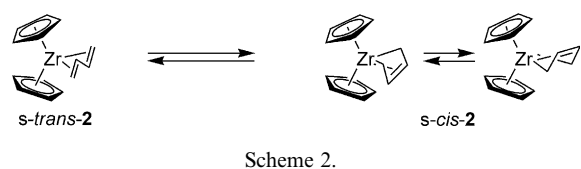
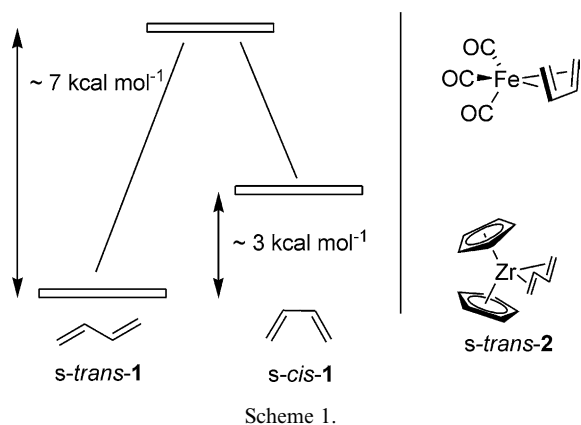
The parent conjugated diene, 1,3-butadiene, is characterized by the presence of an equilibrating pair of rotational isomers, namely *s-trans*-butadiene (*s-trans*-**1**) and *s-cis*-butadiene (*s-cis*-**1**). The transoid conformer is by ca. 3 kcal mol⁻¹ is more stable. The activation energy of the *s-trans*-**1** to *s-cis*-**1** interconversion amounts to ca. 7 kcal mol⁻¹ (see Scheme 1) [1]. Most transition metal fragments, however, favor η^4 -coordination to the less favorable *s-cis*-C₄H₆ isomer, probably because of a better orbital overlap. The first example of a stable isolable

(*s-trans*- η^4 -butadiene)metal complex was (butadiene)zirconocene (*s-trans*-**2**) that was independently discovered and described by our research group and by Nakamura and Yasuda et al. [2,3]. Since then many examples of this unusual type of complexes have been described for various metal–ligand combinations, and specific bonding features of the (*s-trans*- η^4 -diene) metallocenes were understood [4].

It was found that various synthetic entries initially led to the (*s-trans*- η^4 -diene)ZrCp₂ isomer [5], that is separated from its iso-energetic (*s-cis*- η^4 -C₄H₆)ZrCp₂ isomer (*s-cis*-**2**) by an activation barrier of $\Delta G_{\text{isom}}^\ddagger$ (283 K) = 22.7 ± 0.3 kcal mol⁻¹ (see Scheme 2). The (*s-cis*- η^4 -diene)ZrCp₂ system itself undergoes a rapid “ring-flip” topomerization process ($\Delta G_{\text{topom}}^\ddagger$ = 12.6 ± 0.5 kcal mol⁻¹) [6].

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The homogeneous metallocene *Ziegler–Natta* catalyst systems are characterized by the presence of a reactive alkylmetallocene cation that is able to repetitively insert α -olefins to build up a polymer chain [7,8]. Usually, these organometallic cations (**4**) are generated by treatment of a neutral dialkylmetallocene with a suitable carbanion-abstractor (e.g., MAO, $B(C_6F_5)_3$, or Ph_3C^+) [9]. We have prepared neutral zwitterionic analogs of such reactive metallocene cations available. The (butadiene)zirconocenes and related systems turned out to be ideal precursors for the development of such zwitterionic (betaine) systems (**5**) [10]. We will describe a variety of such examples in this account and discuss some of their typical features (cf. Scheme 3).

2. Reactions of the (butadiene)zirconocenes with electrophiles

The system of rapidly equilibrating (butadiene)zirconocene isomers reacts rapidly with a variety of organo-

ic electrophilic reagents. Usually, the actual reaction proceeds by means of a bimolecular reaction of the reactive (η^2 -butadiene)zirconocene intermediate **3** (see Scheme 4). A typical example is the reaction of the 2/3 system with ketones. The reaction is probably initiated by vinyloxametallacyclopentane (**6**) formation, followed by a rearrangement to yield the respective oxazirconacycloheptene isomers **7** that are usually isolated. Fig. 1 shows the X-ray crystal structure analysis of a typical example, here the 1:1 reaction product of (butadiene)zirconocene with benzophenone [11]. In some cases, a second equivalent of, e.g., the diarylketone is subsequently added to yield **8** [12].

Metal carbonyls react similarly with (butadiene)zirconocene. In the majority of the cases examined, a

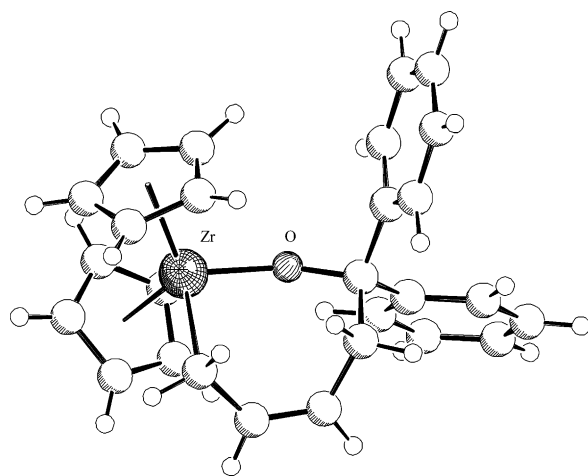
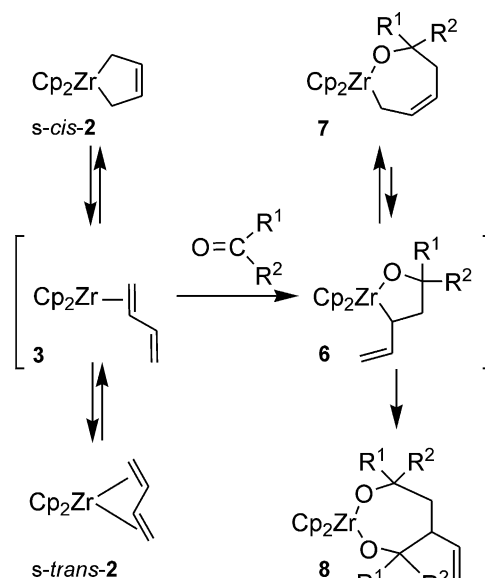
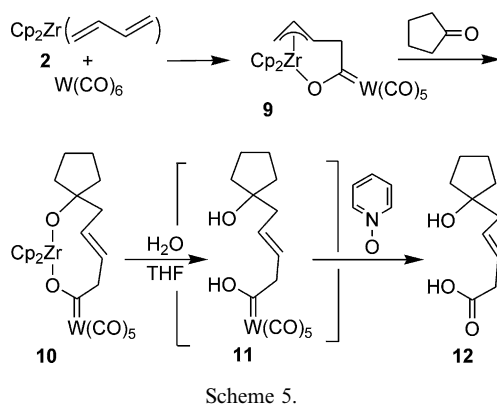


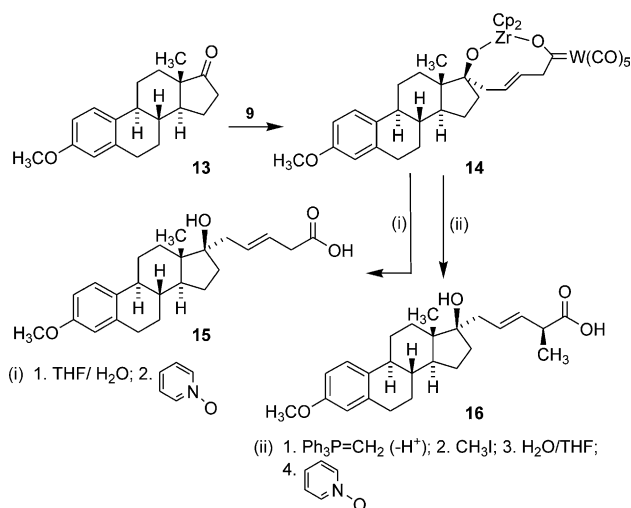
Fig. 1. Molecular structure of the benzophenone addition product to (butadiene)zirconocene (**7**, $R^1 = R^2 = Ph$).



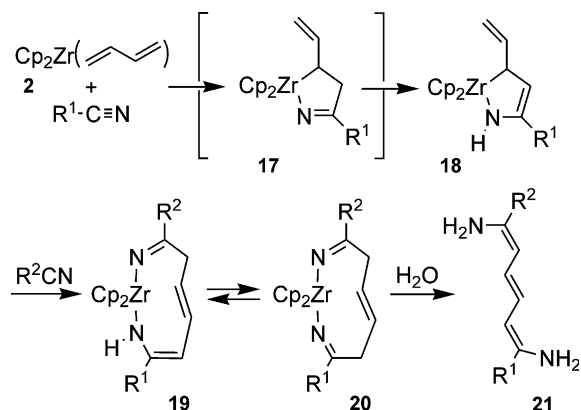
metallacyclic (π -allyl)zirconoxycarbene complex was isolated (and often characterized by X-ray diffraction). A typical example is the reaction of **2** with $W(CO)_6$ that gave product **9** in high yield. This subsequently added a variety of ketones or aldehydes to give nine-membered metallacycles, for example the reaction of **9** with cyclopentanone to yield **10**. The addition of a mild oxidant (e.g., pyridine-*N*-oxide) followed by hydrolysis cleanly yielded the corresponding ϵ -hydroxy-*trans*-3-hexenoic acid (here **12**). This degradation reaction probably proceeds via a reactive hydroxy carbene tungsten complex (**11**) generated by selective hydrolysis of **10** (see Scheme 5) [13].

We have used this template reaction that essentially couples butadiene, a ketone and an organometallic CO_2 equivalent at the zirconocene framework in organic synthesis. A representative example is the construction of steroid side chains that was carried out, e.g., at a steroid framework starting from the 3-methoxyestrone derivative **13** [14] (see Scheme 6).

In a similar reaction, two nitriles were 1,4-coupled with butadiene at the zirconocene template to eventually



Scheme 6.



Scheme 7.

yield stable 1,6-diaminohexatriene products. Again, a series of five- and nine-membered metallacycles were found to be involved as the essential intermediates and organometallic products in this coupling reaction. The primary enamines **21** are thermodynamically favored over their imine tautomers, as was shown for a number of examples using various types of substituents R^1 and R^2 [15] (see Scheme 7).

3. The (butadiene)metallocene/ $B(C_6F_5)_3$ systems

The (butadiene)zirconocene system also adds a variety of inorganic or main group organometallic electrophiles at a terminal conjugated diene carbon atom. Under kinetic control, the strong Lewis acid $B(C_6F_5)_3$ adds to either of the parent (η^4 -butadiene) $ZrCp_2$ isomers (**2**) to generate a cisoid η^3 -allyl-type zwitterionic zirconocene cation (μ -hydrocarbyl)borate anion product (**23**) that was identified by NMR spectroscopy at low temperature. Either of the (η^4 - C_4H_6) $ZrCp_2$ isomers yields exclusively this cisoid addition product under kinetic control, which indicates that the $B(C_6F_5)_3$ Lewis acid catalyzes the (*s-cis*/*s-trans*- η^4 -butadiene) $ZrCp_2$ isomerization, presumably via a reactive zwitterionic (σ -allyl)metallocene intermediate, such as, e.g., **22**. Under thermodynamic control, at room temperature, the rapid isomerization of **23** (probably via **22**) is observed and the metallacyclic transoid π -allyl betaine product (**24**) was isolated in good yield. Complex **24** features a bridging F-C(Ar) moiety to zirconium that shows up in the ^{19}F NMR spectrum (δ -213) as well as the X-ray crystal structure analysis of **24** (see Fig. 2) [16] (see Scheme 8).

Complex **23** was too labile to be isolated, but sterically more demanding *ansa*-metallocene analogs of this structural type turned out to be sufficiently stable at ambient temperature to allow their isolation and characterization by X-ray diffraction [17]. A third structural betaine type was experimentally detected

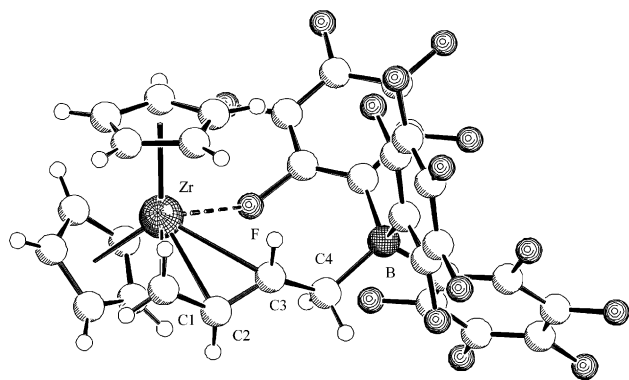
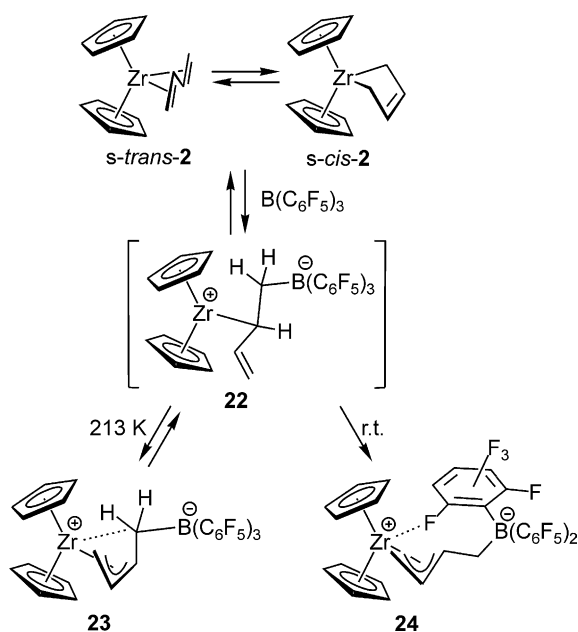


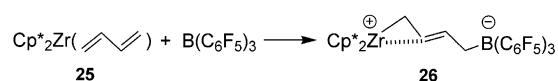
Fig. 2. A view of the molecular structure of the zwitterionic complex **24**. Selected analytical data: Zr–C1 2.339 Å, Zr–C2 2.494 Å, Zr–C3 2.528 Å, Zr–F 2.423 Å; Zr–F–C_{Ar} 140.0°; $\delta^{19}\text{F} = -213$ ppm.



Scheme 8.

when (η^4 -butadiene)bis(pentamethylcyclopentadienyl) zirconium (**25**) was treated with $\text{B}(\text{C}_6\text{F}_5)_3$. The resulting addition product (**26**) showed an unusual very distorted σ,π -allyl-type structural subunit, marking some point on the pathway along the conversion from a π -allyl to a purely σ -allyl structural type [18] (cf. Scheme 9).

As expected the F–C(Ar) coordination in complex **24** can readily be cleaved, e.g., by the addition of suitable donor ligands. Thus, PMe_3 adds cleanly to **24** to yield the open zwitterionic adduct (**28**) [19]. The analogous hafnium complex **24'** even added one equivalent of carbonmonoxide to yield the stable d^0 -metal carbonyl complex (**27**) [16]. Both the complexes **27** and **28**, respectively, featured a distorted π -allyl coordination to the early metal center that was revealed by their X-ray crystal structure analyses (cf. Fig. 3).



Scheme 9.

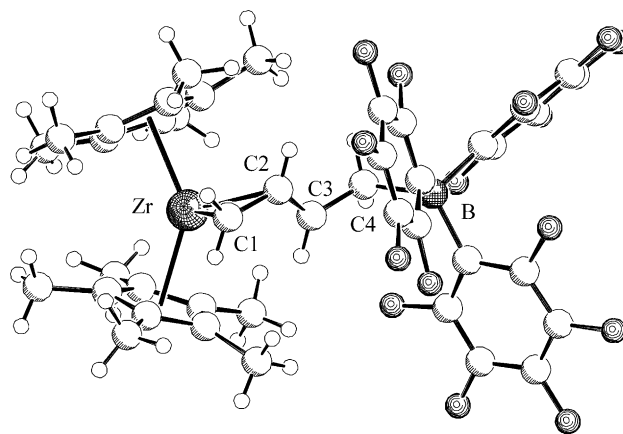
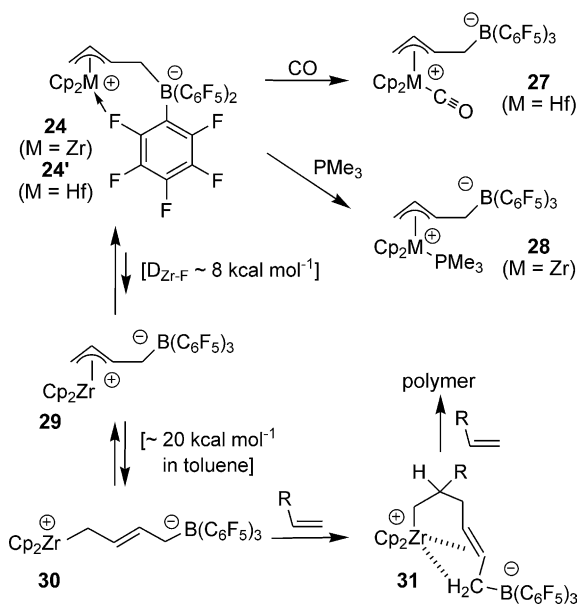


Fig. 3. Molecular structure of the σ,π -allyl-type betaine system **26**. Selected bond lengths: Zr–C1 2.337 Å, Zr–C2 2.487 Å, Zr–C3 2.722 Å, Zr–C4 3.856 Å.

The Zr···F–C(Ar) bond dissociation energy in **24** is ca. 8 kcal/mol. This was revealed from the *o*-fluorine ^{19}F NMR decoalescence at low temperature. The subsequent π -allyl/ σ -allyl zirconocene interconversion (**29/30**) is much slower (ca. 20 kcal/mol) as judged from the dynamic ^1H NMR spectrum of this system. We must, therefore, assume that the coordinatively unsaturated zirconocene σ -allyl borate betaine system (**30**) is available as a reactive intermediate at room temperature from the equilibrium with **24** and **29**, respectively (see Scheme 10). Consequently, the system reacts readily with α -olefins. At low temperatures (ca. -10°C), one equivalent of ethylene or an 1-alkene is inserted into the remaining metal to carbon bond to form the mono-olefin-insertion products **31**. These systems are very sensitive. They could only be characterized by NMR spectroscopy, but not isolated. The spectroscopic analysis revealed that the compounds **31** are likely to feature a weak coordination between the C=C double bond and the d^0 -metal center plus an internal ion pair interaction of Zr^+ with the $-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$ end of the betaine chain [20]. Increasing the temperature slightly (ca. 0°C) in the presence of excess alkene subsequently leads to the formation of the respective polyolefin. We must, therefore, probably regard the complexes **31** as reactive intermediates at an early stage of the initiation sequence of the polymerization reaction at the zwitterionic homogeneous metallocene Ziegler–Natta catalysts **24**.

Examples of the complex type **24** were obtained for a great variety of open Group 4 metallocene frameworks, of *ansa*-metallocenes and of a number of “constrained



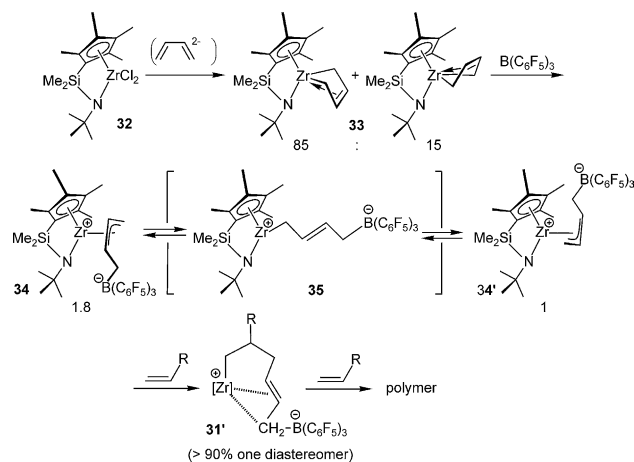
Scheme 10.

geometry” Cp/amido Ti, Zr, and Hf systems. All these zwitterionic systems proved to be reactive olefin polymerization catalysts that did not require additional activating components (although the presence of a H_2O scavenger was often technically helpful).

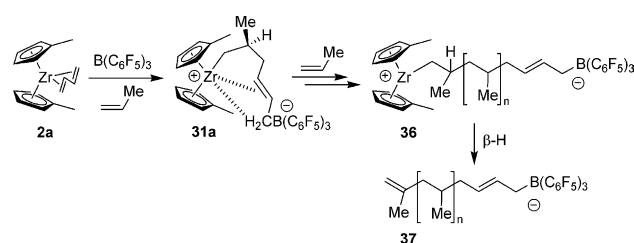
The new (lig)M– C_4H_6 – $\text{B}(\text{C}_6\text{F}_5)_3$ systems showed activities similar to the respective (lig) MCl_2 /MAO catalysts [17].

The “constrained geometry” metal dichloride **32** was treated with (butadiene)magnesium to give an 85:15 mixture of the (*s-cis*- C_4H_6) metal complex isomers (prone-/supine-**33**). Their treatment with $\text{B}(\text{C}_6\text{F}_5)_3$ subsequently yielded a 1.8:1 pair of the related cisoid π -allyl betaines (**34/34'**) that interconverted on the NMR time scale probably via the σ -allyl-betaine intermediate **35**. Treatment of the system with an α -olefin at low temperature then resulted in the formation of the metallacyclic mono-alkene insertion intermediate (**31'**), followed by polyolefin formation at slightly higher temperatures (see Scheme 11).

Actually, the initial growth of a polymer chain can experimentally be observed indirectly using the new zwitterionic systems **24**. Here is a typical example. Treatment of the open, nonbridged (butadiene)metallocene starting material **2a** (see Scheme 12) with $\text{B}(\text{C}_6\text{F}_5)_3$ gave the respective betaine catalyst. Its reaction with propene initially gave **31a** at low temperature. Subsequently, additional propene was repetitively inserted into the Zr–C bond of **31a** and its follow-up products to give the initial zwitterionic polymers (**36**). Chain transfer at the end of the initiation sequence furnished the respective anionic polymers **37** that were actually experimentally observed by negative ion electrospray mass spectrometry (ESMS) [10].



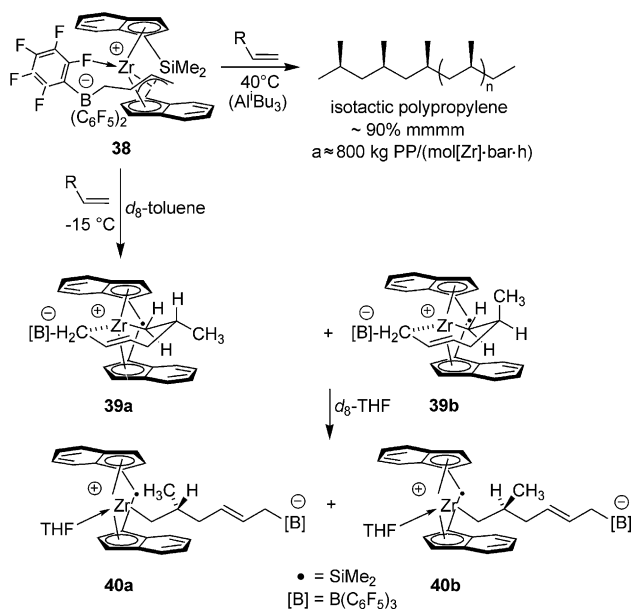
Scheme 11.



Scheme 12.

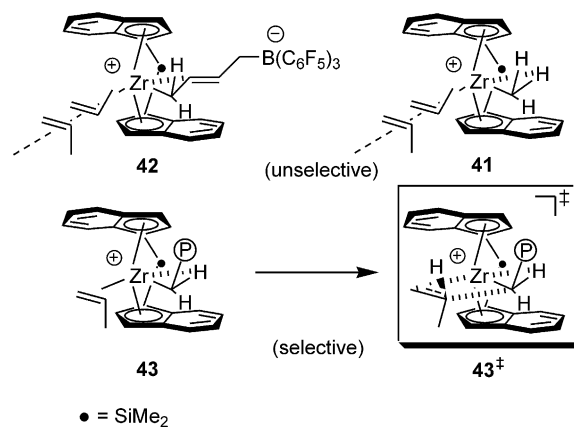
The characterization of the initial alkene insertion product revealed how the stereochemical information was actually transferred from a chiral bent metallocene backbone to the growing α -olefin-polymer chain. For this study, we have prepared the metallocene–butadiene–borate betaine system **38** by treatment of the respective (butadiene) *rac-ansa*-zirconocene complex with $\text{B}(\text{C}_6\text{F}_5)_3$. Addition of propene at 40°C resulted in the rapid formation of isotactic polypropylene (ca. 90% mmmm) as expected. At -15°C in d_8 -toluene, the betaine **38** cleanly inserted one propene molecule to give a 60:40 mixture of two metallacyclic stereoisomers (**39a**, **39b**) that were subsequently opened by the addition of d_8 -THF to yield the open monopropene insertion products (**40a**, **40b**) again in a 60:40 mixture [21] (see Scheme 13).

This experiment (and a similar study carried out by Brintzinger and coworkers [22]) indicates that the transfer of the chirality information from the metallocene backbone is taking place by means of a relay mechanism. The stereoselective 1-alkene polymerization requires that an auxiliary chiral carbon center at the α -position of the growing chain is built up (**43** in Scheme 14), the stereochemistry of which is controlled by the metallocene backbone. It is this carbon-chirality center that then effectively controls the Re/Si differentiation of the incoming prochiral α -olefin. The auxiliary carbon center itself is consumed



Scheme 13.

in each olefin insertion step and an equivalent chiral auxiliary is built up concertedly from the CH_2 -terminus of the inserted 1-alkene. A very detailed mechanistic study [23] has revealed that the olefin addition step must probably be regarded as a (reversible) pre-equilibrium step in the overall sequence, so that stereochemistry is actually controlled in the subsequent olefin-insertion step (i.e. at the stage of the transition state 43^\ddagger).

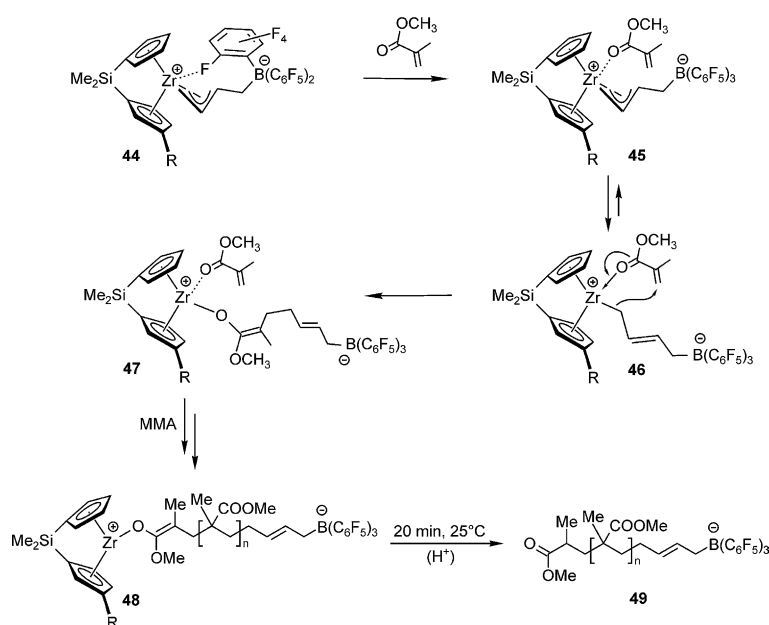


Scheme 14.

4. Polymerization of a functionalized olefin

Some metallocene catalysts have also been used for methylmetacrylate polymerization [24]. We have used the butadiene complex of a series of Me_2Si -bridged *ansa*-zirconocenes. Treatment with $B(C_6F_5)_3$ converted them to the zwitterionic systems **44** that were active MMA polymerization catalysts. For the parent system **44a** ($R = H$), we were able to actually observe the initial methylmetacrylate addition product (**45**) by NMR.

A subsequent series of *Michael* addition reactions via Zr-ester enolates then resulted in polymer chain growth by means of a living polymerization to probably yield products **48**. Their hydrolysis then gave rise to a polymer distribution of the PMMA derivatives **49** that were



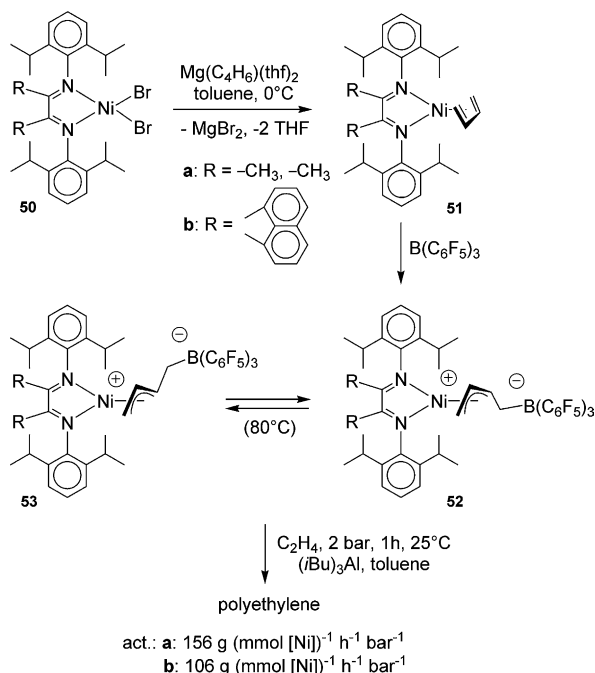
Scheme 15.

detected and analyzed by anion electrospray mass spectrometry [25] (see Scheme 15).

5. Late transition metal systems

Chelate bis(imine) complexes of a variety of metals from the right side of the periodic table have become quite important in homogeneous *Ziegler–Natta* catalysis [26]. Addition of $B(C_6F_5)_3$ to the bis(imine)nickel(butadiene) complexes **51** [27] initially gave the cisoid zwitterionic π -allyl complexes **52**. These were stable at room temperature, but rapidly rearranged to the transoid isomers **53** upon heating (see Scheme 16). Both the complexes **52a** and **52b** gave active ethene polymerization catalysts when exposed to the olefin (2 bar) in toluene solution in the presence of tri(isobutyl)aluminum [28]. However, it appeared that in these cases, the complexes **52** were not the intrinsic catalysts, in contrast to their Group 4 bent metallocene analogs, but required the presence of the trialkylaluminum agent for in situ activation (cf. Fig. 4).

We have reacted the bis(imino)pyridine cobalt (II) complexes **54** ($R = CH_3$ or Ph) with (butadiene)magnesium [29]. From this reaction, we were not able to isolate the corresponding butadiene complexes, instead the reaction proceeded with reduction to the corresponding bis(imino)pyridine cobalt (I) halides (**55**). A similar reduction reaction had previously been observed by Gal et al. and Gibson et al. [30], when **54a** ($R = CH_3$) was treated with, e.g., methyl lithium. The reaction of



Scheme 16.

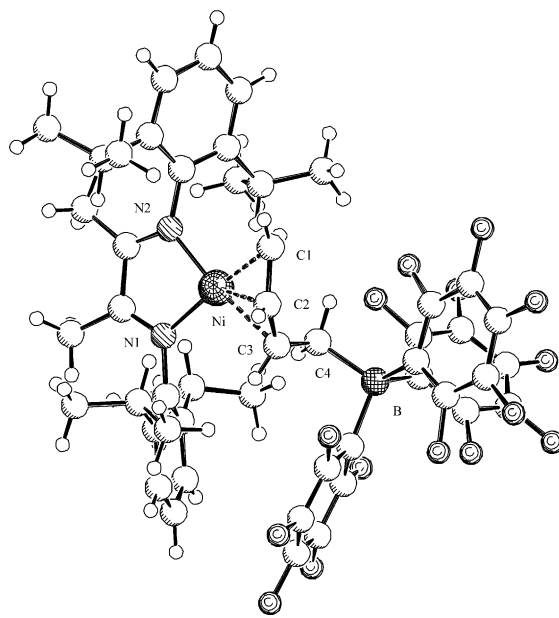
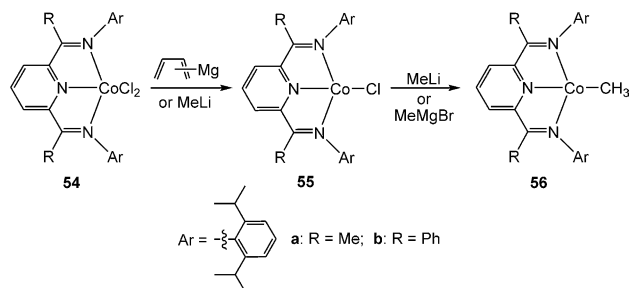


Fig. 4. A view of the molecular structure of the zwitterionic nickel complex **52a**. Selected bond lengths: Ni–C1 2.007 Å, Ni–C2 1.968 Å, Ni–C3 2.048 Å, Ni–C4 2.803 Å.

54 with excess MeLi or **55** with MeLi or MeMgBr resulted in the formation of the bis(imino)pyridine cobalt (I) methyl complexes **56**. The complexes **56** themselves were inactive towards ethene under our conditions, but treatment of the bis(imino)pyridine cobalt(I)CH₃ complexes (**56**) simply with $Li[B(C_6F_5)_4]$ under ethene gave rise to a low activity polyethylene formation.[31] In view of this surprising result, we cannot exclude that the very low activity polyethylene formation which we had previously observed [29] in the **55**/ $Li[B(C_6F_5)_4]$ systems might actually have been caused by some unidentified metal alkyl contaminants. The nature of the observed polymerization reaction in the **56**/ $Li[B(C_6F_5)_4]$ system is mechanistically unclear at present [30,32]. Such low activity polymer formation may be an intrinsic feature of the system actually looked at, but cannot be ruled out to arise from a small amount of a very active catalyst generated from an unidentified minor contamination (cf. Scheme 17).



Scheme 17.

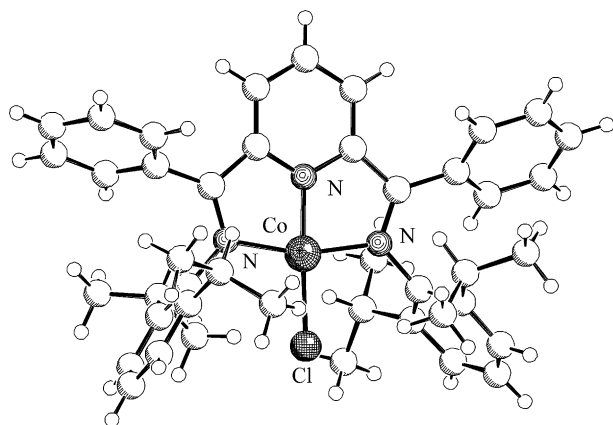


Fig. 5. Molecular structure of complex **55b**, obtained from the reaction of **54b** with (butadiene)magnesium.

6. Some conclusions

The butadiene/ $B(C_6F_5)_3$ route to active metallocene Ziegler–Natta catalyst systems provides an interesting alternative to other activation pathways. A great variety of open bent metallocene frameworks, of *ansa*-metallocenes, and of related constrained geometry systems form stable and isolable butadiene complexes that add the Lewis acid $B(C_6F_5)_3$ at a terminal butadiene carbon atom. The resulting zwitterionic Group 4 metal complexes are active α -olefin polymerization catalysts without the need for further activation. Of special value and importance was the ability of many such systems to serve as ideal substrates in a variety of mechanistic studies of the selective carbon–carbon coupling reactions that rapidly take place at such metallocene catalyst systems. The number of the systems studied in detail probably represent some of the closest experimental models of the actual, very active homogeneous Ziegler–Natta catalysts known so far, be it in unfunctionalized 1-alkene polymerization or even in the polymerization of the functionalized olefin methylmetacrylate (see Fig. 5).

Acknowledgments

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