

# Some selected chapters from the (butadiene)zirconocene story

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## Abstract

(Butadiene)zirconocene was the first mono-nuclear metal complex for which the *s-trans*- $\eta^4$ -conjugated diene coordination mode was established. Meanwhile a variety of additional examples from metals throughout the Periodic Table was found. The (butadiene)zirconocenes have found use as valuable reagents in organic and organometallic synthesis, for which various representative examples are described. They have also found extensive use as precursors for the generation of very active and sometimes very selective homogeneous metallocene Ziegler–Natta olefin polymerization catalysts. The employment of the dipolar zirconocene(butadiene)/ $B(C_6F_5)_3$  addition products in mechanistic studies has revealed important aspects of the reaction course taken in the carbon–carbon coupling reaction sequences at this important class of catalysts. Several specific examples are described in this article.

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**Keywords:** Zirconocene; Conjugated dienes; Template reactions; Olefin polymerization catalysts; Mechanistic studies

## 1. Introduction

The smallest conjugated di-olefin, 1,3-butadiene, features two equilibrating planar, or close to planar conformations. Of these, the *s-trans*-butadiene (*s-trans*-**1**) is the global minimum. It is separated by an energy barrier of  $\Delta G^\ddagger \approx 7 \text{ kcal mol}^{-1}$  from the less favoured *s-cis*-butadiene conformer (*s-cis*-**1**). The latter is by ca. 3 to 4 kcal  $\text{mol}^{-1}$  less stable (see Scheme 1) [1].

The situation is quite different when 1,3-butadiene is coordinated to a transition metal. Most metal complex fragments electronically favour  $\eta^4$ -coordination of the less stable *s-cis*-butadiene conformation to make use of a good spatial overlap of the available metal orbitals with the conjugated diene  $\pi$ -electron system.

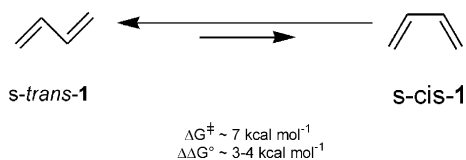
Therefore, it was a surprise when reports about the first stable and isolable mononuclear ( $\eta^4$ -*s-trans*-butadi-

ene) metal complexes appeared [2–4]. It became clear that the special electronic features of the Group 4 metallocenes [5] were able to favour coordination of the more linearly oriented *s-trans*-conjugated diene framework as opposed to the majority of other metal complex fragments used in organometallic chemistry.

We had prepared (*s-trans*- $\eta^4$ -butadiene)zirconocene (*s-trans*-**2**) by the reaction of 1,3-butadiene with  $Cp_2Zr$ , that was in situ generated by photolysis of diphenylzirconocene [2]. Independently, Yasuda et al. [3] had obtained the same compound from the reaction of zirconocene dichloride with the “butadiene–magnesium” reagent. There was evidence that both methods primarily led to the formation of a reactive ( $\eta^2$ -butadiene)zirconocene intermediate (**3**) that stabilized itself by rearrangement to *s-trans*-**2** under kinetic control, but also gave rise to the formation of the (*s-cis*- $\eta^4$ -butadiene) $ZrCp_2$  isomer (*s-cis*-**2**) under equilibrium conditions [6]. Eventually, a close to 1:1 mixture of (*s-trans*-) and (*s-cis*-butadiene)zirconocene was found under thermodynamic control. The *s-cis*-**2** isomer is characterized by a  $\sigma, \pi$ -metallacyclic structural framework that undergoes a

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Scheme 1. The *s-trans*/*s-cis*-butadiene equilibrium.

“ring-flip” automerization process, that is rapid on the NMR time scale (see Scheme 2) [4].

## 2. The (*s-trans*- $\eta^4$ -butadiene)metallocene structural problem

The detailed structural characterization of the (*s-trans*- $\eta^4$ -butadiene)zirconocenes was hampered for many years by severe disorder problems of the examples investigated. Although systems with substituted *s-trans*-conjugated diene ligands had shown to behave well in their structure determination [7], it took some time to solve this problem for systems featuring the parent *s-trans*- $\eta^4$ -butadiene coordination.

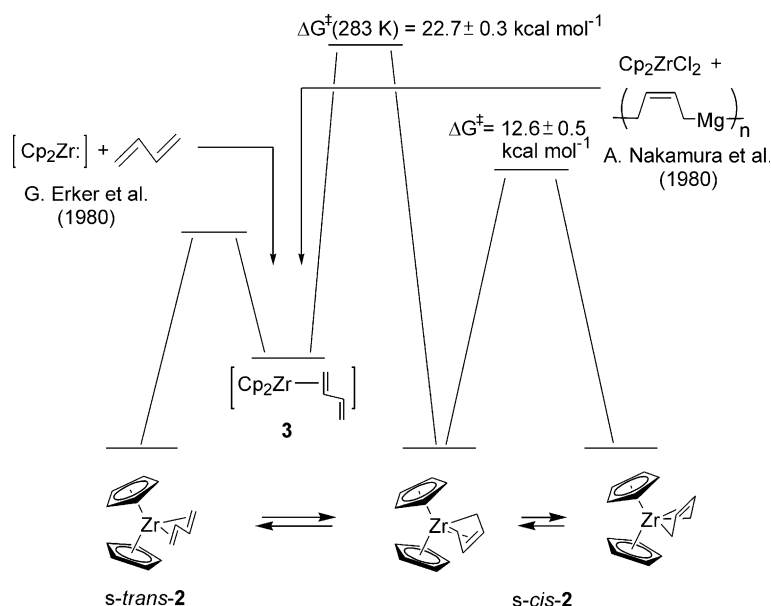
A stereochemical “trick” helped. Treatment of the chiral *ansa*-zirconocene dichloride **4** with butadiene–magnesium gave the corresponding butadiene complexes (**5**) [8]. Due to the combination of the chiral  $C_2$ -symmetric bent metallocene backbone with the planarly-chiral (*s-trans*- $\eta^4$ -butadiene)Zr building block two diastereoisomeric (*s-trans*- $\eta^4$ -butadiene) *ansa*-zirconocene complexes occur (*s-trans*-**5** and *s-trans*-**5'**) in addition to an equilibrating pair of (*s-cis*-diene)metallocene isomers (*s-cis*-**5**). In this specific case formation of all three complexes was actually observed (see Scheme 3). Single crystals were obtained from the major diastereoisomer that

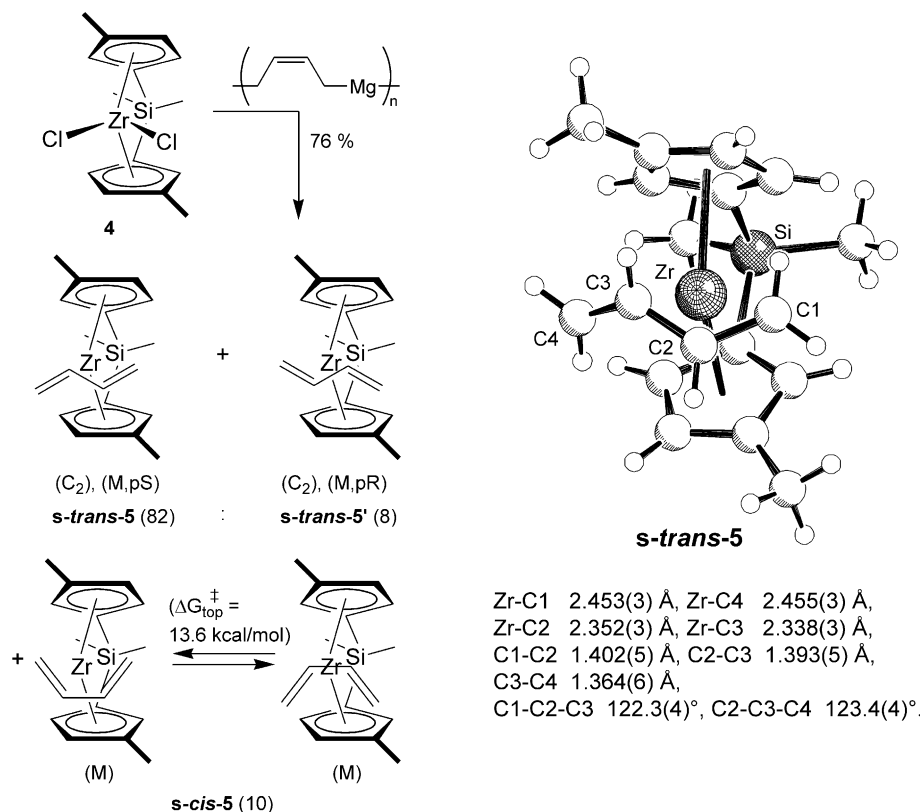
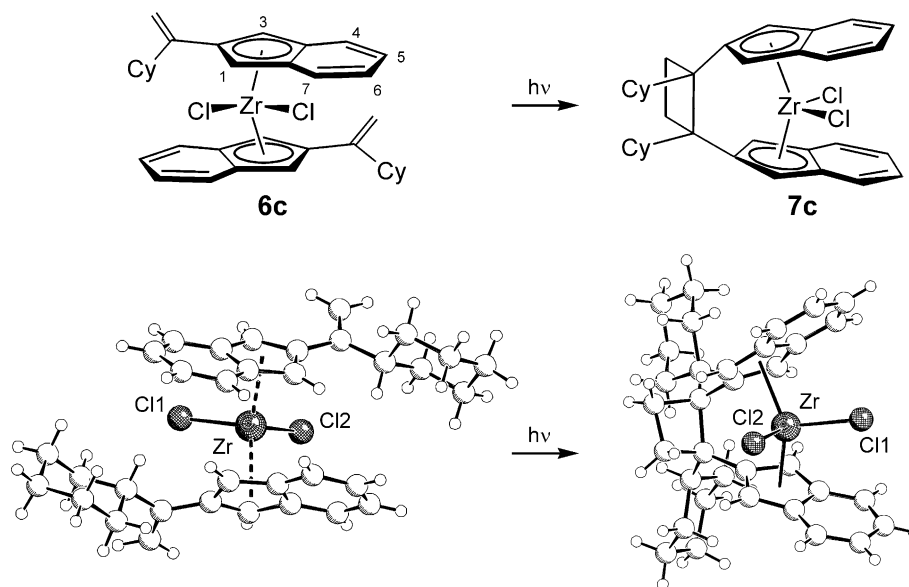
allowed a detailed description of the (*s-trans*- $\eta^4$ -butadiene)Zr structural parameters by X-ray diffraction. This coordination type is characterized by rather short internal C2/C3–Zr distances (by ca. 0.1 Å shorter than the external C1/C4–Zr bonds), a close to equidistant C1–C2–C3–C4 framework and a torsional angle between the two C=C double bonds of 124.3(4)° ( $\theta$  C1–C2–C3–C4) [8].

We have recently prepared a special new *ansa*-metallocene framework to selectively accommodate the *s-trans*- $\eta^4$ -butadiene ligand. Treatment of 2-alkenylinde-nyl ligands with  $ZrCl_4$  yielded the respective open, non-bridged metallocenes **6** (e.g., R = methyl (**a**), phenyl (**b**), or cyclohexyl (**c**)). Photolysis of these systems resulted in a rapid, efficient and practically complete intramolecular [2 + 2] cycloaddition to yield the respective cyclo-butylene-bridged *ansa*-zirconocene dichlorides **7** (see Scheme 4) [9].

Treatment of **7a** (R = CH<sub>3</sub>) with butadiene–magnesium gave a single (*s-trans*- $\eta^4$ -butadiene)zirconocene complex (**8**). Its <sup>1</sup>H NMR spectrum (see Scheme 5) revealed a pronounced shift of the H<sub>meso</sub>-resonance to lower  $\delta$ -values ( $\Delta\delta \approx -4.5$  ppm). This indicates that the meso-butadiene hydrogens are located above the phenylene rings of the spatially fixed indenyl ligand systems.

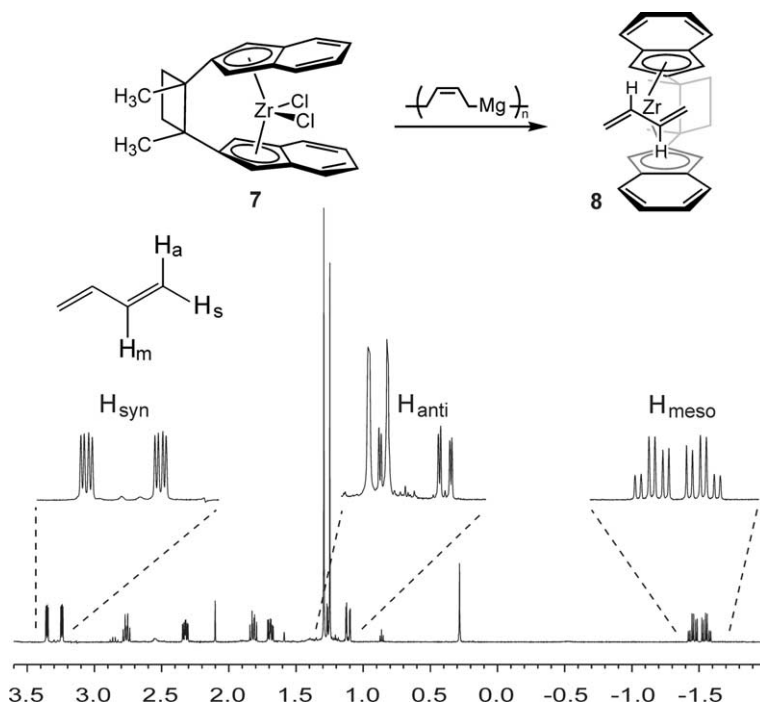
We assume that the energy gain of the resulting (butadiene)C–H/ $\pi$ -arene interaction [10] is sufficient to shift the equilibrium completely to the (*s-trans*- $\eta^4$ -butadiene) metallocene coordination side. We will see whether the arrangement of this or other ligands at the bent metallocene front side within the “ $\pi$ -electron-cage” of this very special *ansa*-metallocene framework will lead to unusual chemical features.

Scheme 2. The (*s-trans*/*s-cis*- $\eta^4$ -butadiene)zirconocene energy profile.

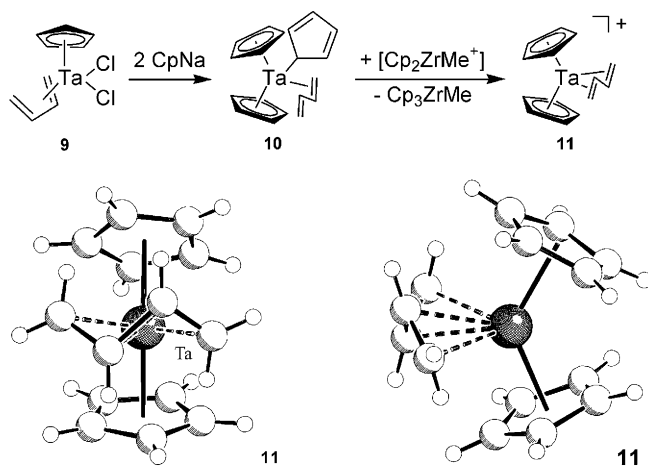
Scheme 3. Formation and structural characterization of the (*s-trans*- $\eta^4$ -butadiene)ansa-zirconocene complex *s-trans*-5.Scheme 4. Photochemical [2 + 2] cycloaddition of bis(2-alkenylindenyl)ZrCl<sub>2</sub> complexes to yield cyclobutylene-bridged ansa-metalloocene complexes.

Meanwhile, the number of examples of (*s-trans*- $\eta^4$ -butadiene) transition metal complexes has increased considerably. This specific structural variety is not limited to the chemistry of the Group 4 bent metallocenes anymore, but can be found as a specific structural element with quite a number of other metal complexes as well. A recent example from our research group is

the (*s-trans*- $\eta^4$ -butadiene)bis(cyclopentadienyl)tantalum cation complex (**11**, and a number of related systems) [11]. Complex **11** was synthesized by treatment of the (butadiene)Ta complex **9** with two equivalents of CpNa followed by a Cp-anion abstraction reaction (using [Cp<sub>2</sub>ZrMe]<sup>+</sup> as the anion abstracting agent, see Scheme 6). Complex **11** was characterized by X-ray diffraction.



Scheme 5. Formation and  $^1\text{H}$  NMR spectrum of the (*s-trans*- $\eta^4$ -butadiene) *ansa*-zirconocene complex **8**.



Ta–C1 2.418(17) Å, Ta–C4 2.497(19) Å, Ta–C2 2.306(15) Å, Ta–C3 2.314(12) Å

Scheme 6. Synthesis and molecular structure of the cationic  $[(s\text{-}trans\text{-}\eta^4\text{-butadiene})\text{TaCp}_2]^+$  complex (only the cations are depicted).

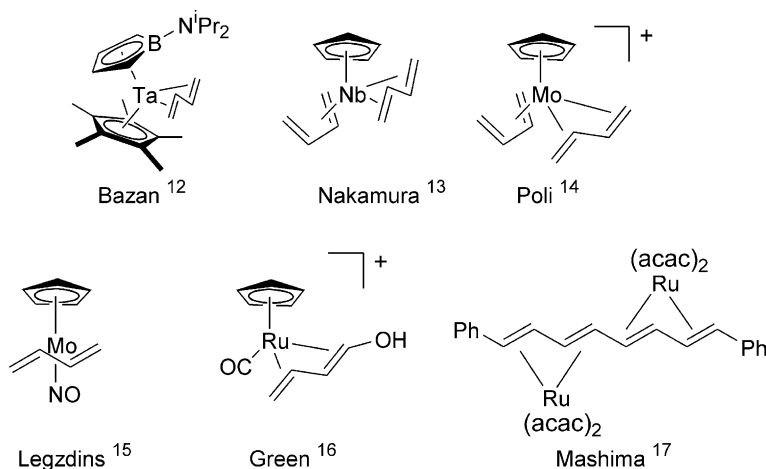
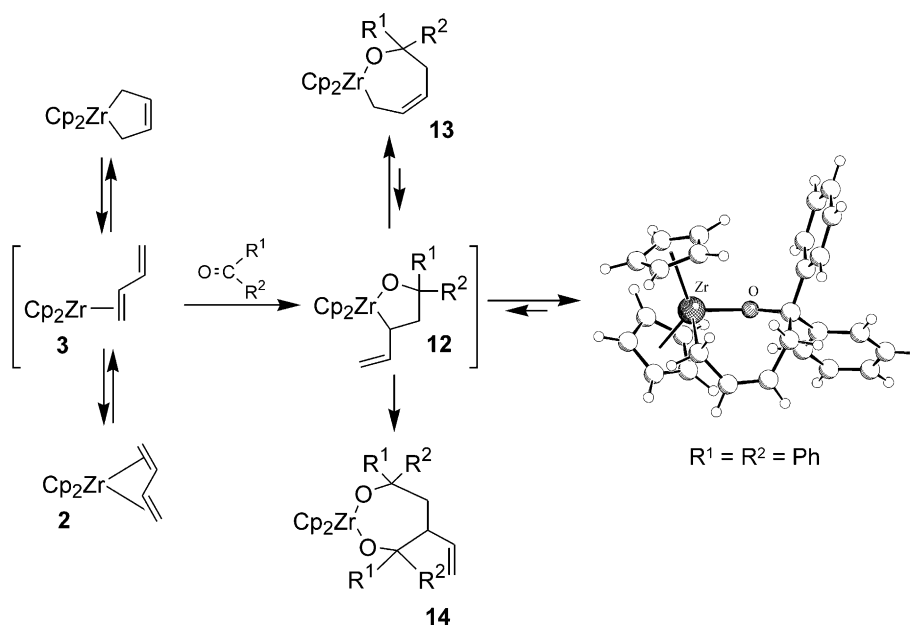
(*s-trans*- $\eta^4$ -Butadiene) complexes have been described from quite a number of metal complex frameworks from d-elements throughout the Periodic Table. A selection of typical examples is depicted in Scheme 7 [12–17].

### 3. Template reactions

Unsaturated reagents are selectively coupled with the butadiene ligand at the zirconocene template. The stable (butadiene)zirconocene isomers (**2**) react via the unsaturated ( $\eta^2$ -butadiene)zirconocene intermediate (**3**). Ketones are in this way coupled with the butadiene

ligand to initially form a metallacyclic ( $\sigma$ -allyl)zirconocene complex (**12**) that is in most cases subsequently stabilized by formation of a metallacyclic seven-membered ring isomer (**13**, see Scheme 8) [18]. In a few special cases an additional CC-coupling reaction with a second ketone equivalent is observed to yield **14** [19].

The reaction of **2** with metal carbonyl complexes takes a similar course. As a typical example, one carbonyl group of  $\text{W}(\text{CO})_6$  is coupled with the butadiene ligand, in this case to form a stable, readily isolated metallacyclic ( $\eta^3$ -allyl)zirconoxycarbene complex (**15**). Similar products were obtained from the reaction of **2** with a great variety of other metal carbonyl complexes

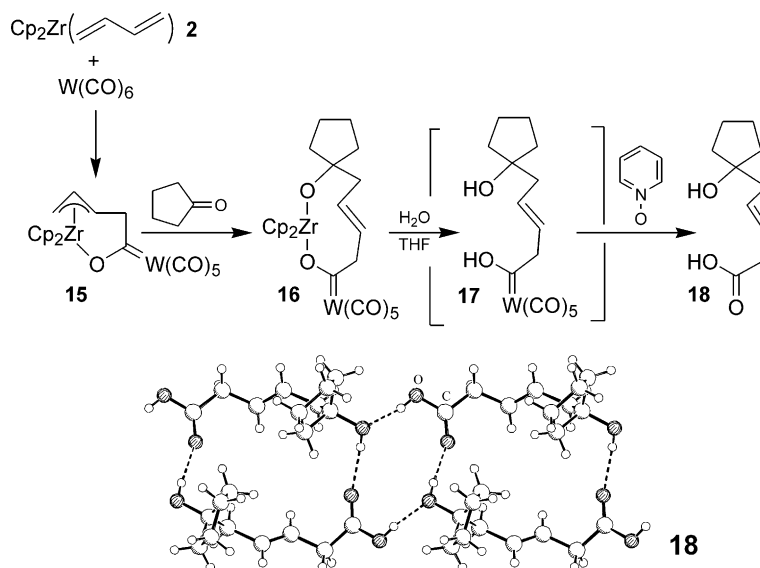
Scheme 7. Various examples of stable, isolated (*s-trans*- $\eta^4$ -conjugated diene) metal complexes.

Scheme 8. Coupling reactions of the (butadiene)zirconocene system with ketones.

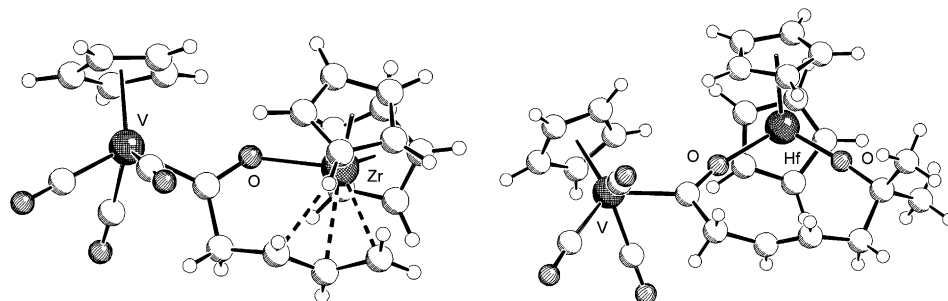
as well (for typical examples see Scheme 10) [20]. The complexes **15** selectively add a ketone with C–C bond formation at the remaining terminal carbon atom of the former butadiene ligand to yield the nine-membered metallacycles **16** (see Schemes 9 and 10). These zirconoxycarbene complexes are then cleaved with water and the in situ generated hydroxycarbene complexes (**17**) oxidized (e.g., by an aminoxide) to yield the  $\epsilon$ -hydroxy-*trans*-3-hexenoic acids (**18**) [21]. Since these organic products have their pair of hydroxy-functional groups separated by a rigid spacer that prevents their intramolecular interaction via hydrogen-bridges, the systems **18** have found use for the construction of organic solid state network structures [22]. It has turned out that the specific structure formed in these arrays depends critically on the nature of the ketone used in the tem-

plate coupling reaction. A suprastructure of a typical example (**18**) is depicted in Scheme 9.

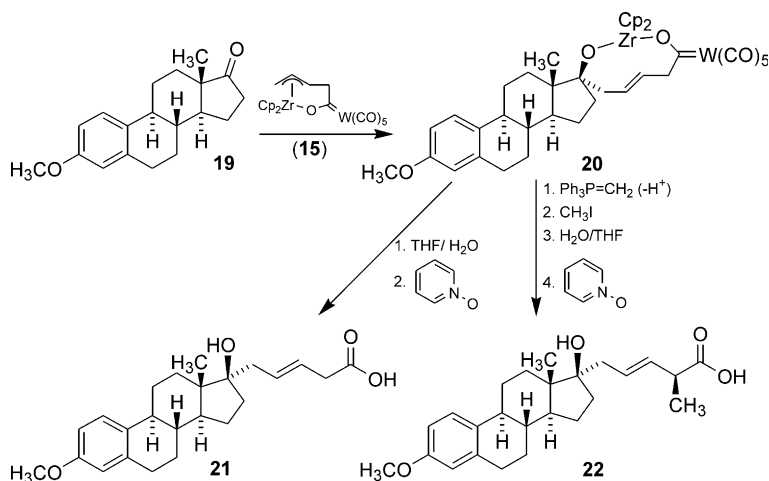
The template reaction was applied in organic synthesis. An example is the reaction of the estron-derivative **19** with the zirconoxycarbene reagent **15** to yield the nine-membered metallacycle (**20**). Hydrolytic/oxidative work-up using the one-pot procedure cleanly gave the derivative **21**, bearing the functionalized C<sub>5</sub>-chain attached at C17 [23]. The rigid framework of **20** has also allowed for a diastereoselective  $\alpha$ -alkylation reaction, in which the chiral metallacyclic ring systems conveys the stereochemical information from the newly formed C17 stereogenic center in a very efficient 1,5-asymmetric induction process [24] that eventually leads to the completely stereoselective formation of the steroid derivative **22** (see Scheme 11).



Scheme 9. Template synthesis of the  $\epsilon$ -hydroxy-*trans*-3-hexanoic acid **18** and a projection of its supra-molecular structure in the solid state.



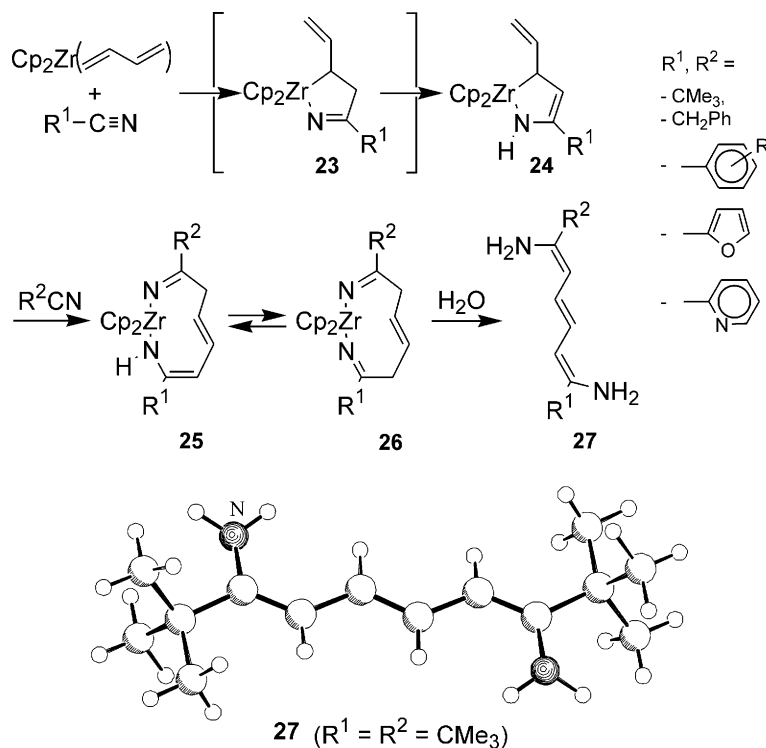
Scheme 10. Views of the molecular structure of two Group 4 metallocyclohexadiene-vanadium complexes prepared by the (butadiene)metallocene template reaction.



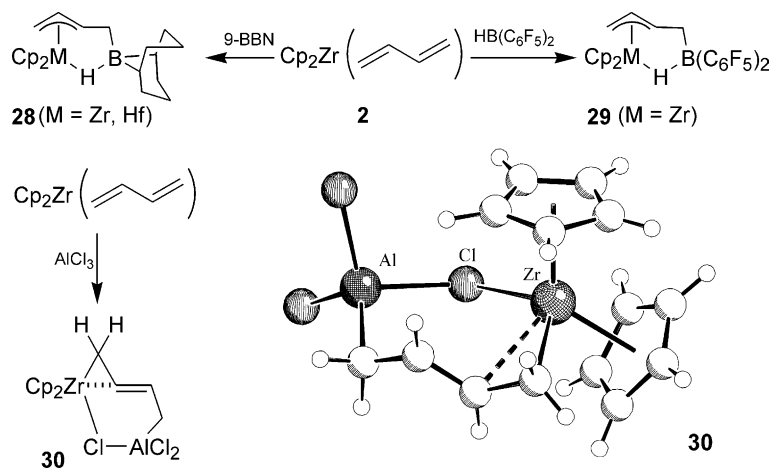
Scheme 11. An example of the application of the template reaction in the stereoselective synthesis of steroid derivatives.

The reaction of the (butadiene)zirconocene system with alkyl- or aryl nitriles takes a similar course. Initially a five-membered metallacyclic  $\sigma$ -allyl zirconocene complex (**23**) is formed. This undergoes a tautomeric equili-

bration (with **24**, see Scheme 12), from which it adds another nitrile equivalent to yield the corresponding nine-membered metallacyclic template coupling product (as a mixture of tautomers, **25/26**). Hydrolytic workup



Scheme 12. The synthesis of the unique 1,6-diamino-hexatriene class of stable, isolable primary enamines **27** by the (butadiene)zirconocene template reaction (the structure of a selected example is depicted).



Scheme 13. Addition products of boron and aluminum reagents to (butadiene)zirconocene.

in this case leads to the formation of the substituted 1,6-diamino-hexatriene products **27**, examples of a unique class of stable primary enamines [25].

#### 4. (Butadiene)zirconocenes in homogeneous Ziegler–Natta catalyst chemistry

(Butadiene)zirconocene reacts with polar inorganic or organometallic X–Y electrophiles in a related way to the addition of olefins, carbonyl compounds or nitriles. The electrophilic part of the reagent is cou-

pled with the butadiene terminus, whereas the adjacent nucleophilic center attains a bridging position in the product with the zirconium atom. Typical examples are the addition products with 9-BBN or HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (see Scheme 13) [26]. Even AlCl<sub>3</sub> adds cleanly to (butadiene)zirconocene. The structure of the respective addition product (**30**) shows a remarkably distorted metallacyclic (allyl)zirconocene geometry which is close to a  $\sigma$ - $\eta^1$ -type of a bonding situation [27].

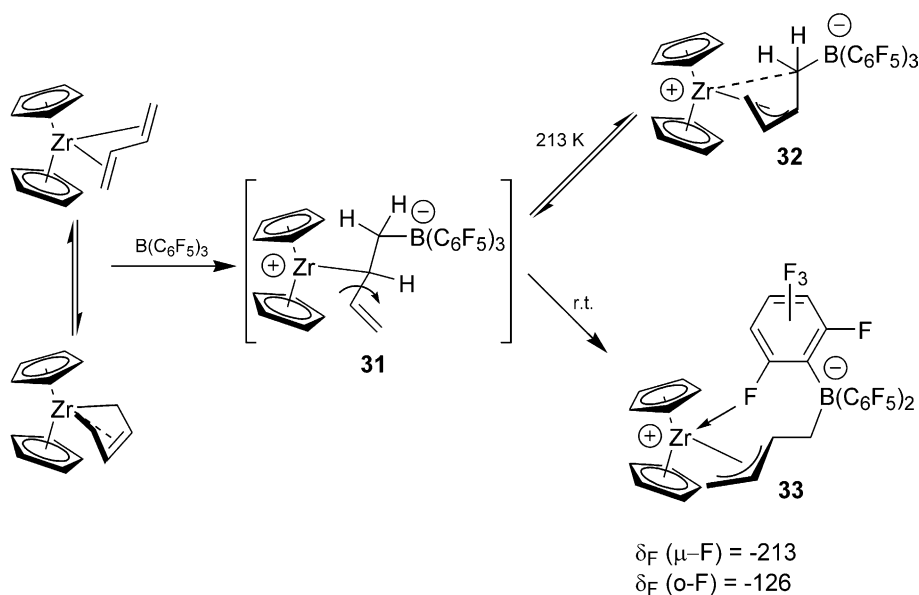
This prompted us to react the (butadiene)zirconocene system (**2**) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [28], a frequently used activa-



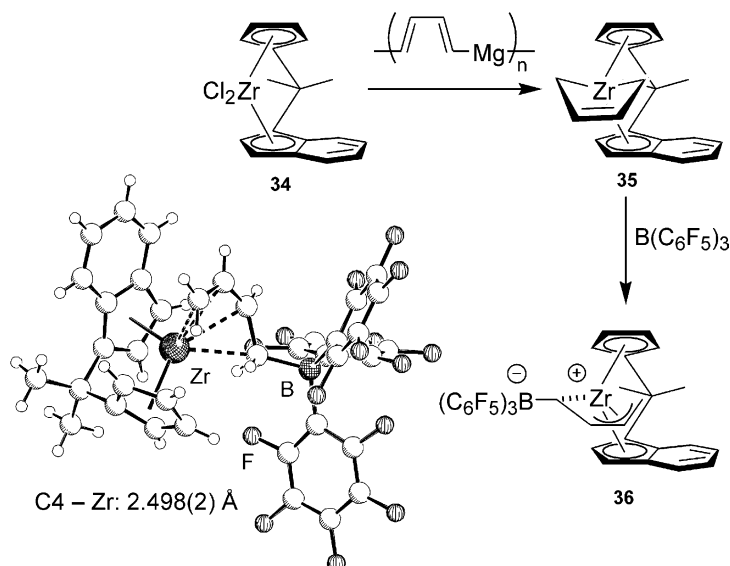
tor component for the generation of active Ziegler–Natta olefin polymerization catalysts [29]. It added cleanly to **2**, but in mechanistic detail differently from the addition reactions described above. There was no indication of the involvement of the ( $\eta^2$ -butadiene)zirconocene intermediate (**3**), but both the (*s-cis*-) and the (*s-trans*- $\eta^4$ -butadiene)zirconocene isomers reacted rapidly with  $B(C_6F_5)_3$  even under conditions that precluded the initial interconversion of the isomers. We assume that a reactive dipolar ( $\sigma$ -allyl)zirconocene complex (**31**) is formed. This reacts exclusively to the *Z*-( $\pi$ -allyl)zirconocene/borane betaine system (**32**) under conditions of kinetic control (see Scheme 14). Warming to room

temperature probably results in the reverse equilibration with **31** and consequently to the formation of the *E*-( $\pi$ -allyl) isomer **33** under thermodynamic control [30].

The *Z*-( $\pi$ -allyl)Zr/B system **32** was not characterized by X-ray diffraction, but we were able to obtain single crystals from the stable *ansa*-metallocene analogue **36** that allowed for an X-ray crystal structure analysis. Complex **36** was obtained by a reaction sequence starting with the “butadiene–magnesium” metathetical exchange reaction with the *ansa*-zirconocene dichloride **34** (see Scheme 15). The resulting (*s-cis*- $\eta^4$ -butadiene)metallocene complex (**35**) was then treated with  $B(C_6F_5)_3$  to yield the stable betaine system **36**. Its

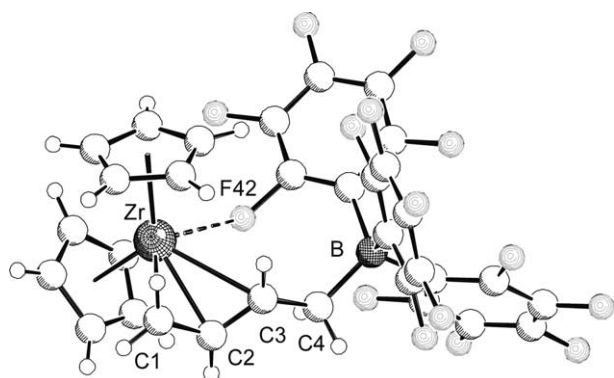


Scheme 14. Reaction of the (butadiene)zirconocene system with  $B(C_6F_5)_3$ .



Scheme 15. Formation and structural characterization of complex **36**.





C1–Zr: 2.339 Å, C2–Zr: 2.494 Å, C3–Zr: 2.528 Å,  
F–Zr: 2.243 Å, Zr–F–C<sub>aryl</sub>: 140.0°,  $\delta^{19}\text{F} = -213$ .

Scheme 16. A view of the molecular geometry of the dipolar zirconocene(butadiene)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> addition product **33**.

X-ray crystal structure analysis revealed the distorted cisoid  $\pi$ -allyl geometry of the C<sub>4</sub>H<sub>6</sub>-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ligand in the dipolar complex and indicated the presence of an internal [Zr]··CH<sub>2</sub>[B] ion pair interaction (C4··Zr: 2.498(2) Å) inside complex **36** [31].

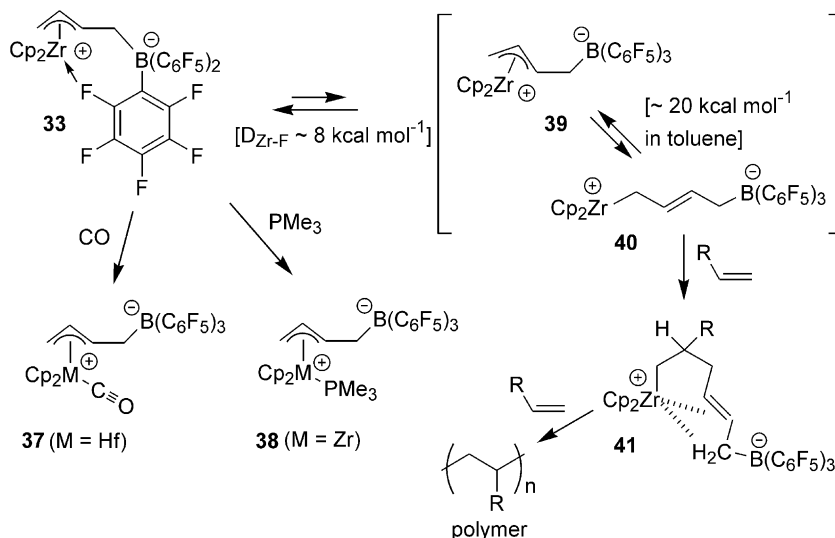
Complex **33** was characterized spectroscopically (including variable temperature NMR spectroscopy) and by X-ray diffraction. The X-ray crystal structure analysis (see Scheme 16) revealed the distorted *E*-( $\pi$ -allyl) coordination of the C<sub>4</sub>H<sub>6</sub>-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ligand. This brings one of the -C<sub>6</sub>F<sub>5</sub> substituents at boron so close to the electrophilic metal center, that a stabilizing Zr–F–C(aryl) linkage is formed. In solution this is maintained and detected at by its characteristic <sup>19</sup>F NMR resonance at low temperature ( $\delta = -213$  ppm) [30,32].

The zirconium–fluorine interaction in complex **33** is rather weak, but certainly in the right order of magni-

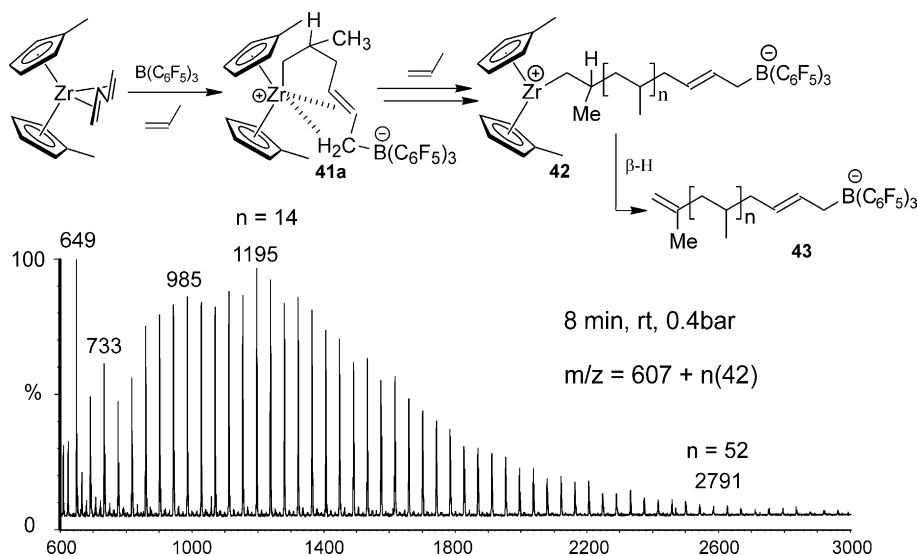
tude to very effectively protect a catalytic center. Consequently, the Group 4 metal–F(C<sub>Ar</sub>) linkage is cleaved by the addition of CO or PMe<sub>3</sub> to yield more stable d<sup>0</sup>(Zr)-donor ligand adducts (**37**, **38**) inside the dipolar metallocene complex frameworks (see Scheme Scheme 17) [30,33].

From the temperature-dependent dynamic NMR spectra the bond dissociation energy of the Zr–F(C<sub>Ar</sub>) linkage was determined at ca. 8 kcal mol<sup>-1</sup>. These spectra further indicated a subsequent, albeit slower  $\pi$ -/ $\sigma$ -allyl equilibration of the C<sub>4</sub>H<sub>6</sub>-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ligand system of complex **33**. It is probably the reactive intermediate **40** that is trapped by added  $\alpha$ -olefins at low temperature to form the respective mono-insertion products (**41**) [34]. These are internally stabilized by a weak olefin  $\pi$ -coordination and an intramolecular ion pair interaction. Raising the temperature in the presence of additional  $\alpha$ -olefin eventually gave rise to the rapid formation of the respective  $\alpha$ -olefin polymer. The mono-insertion product (**41**) is probably to be regarded the first intermediate in the initiation sequence at the active olefin polymerization precursor **33**. These systems consequently represent some of the closest model systems of active homogeneous Ziegler–Natta catalysts known so far.

Chain growth at the active zirconium center of the systems **33** during the catalytic initiation period can actually be followed by electrospray-MS. Treatment of (MeCp)<sub>2</sub>Zr(butadiene) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> followed by propene addition gave rise to chain growth within the dipolar framework. Further propene insertion competed with chain transfer after each individual olefin insertion step, which resulted in the formation of a typical distribution of anionic oligomers (**43**) that was detected by ES-MS (see Scheme 18) [35]. The easily observable



Scheme 17. Reactions of the zirconocene(butadiene)/borane betaine system **33**.



Scheme 18. Electrospray-MS of the oligomeric anion series obtained by repetitive propene insertion into the active Ziegler–Natta catalyst precursor **41**.

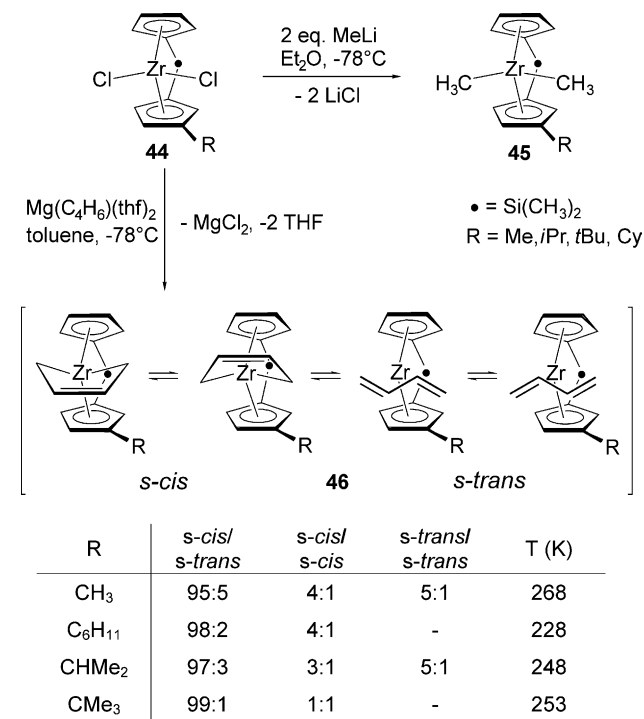
formation of the mono-olefin insertion products (**41**) has also been used to determine a variety of mechanistic features of this essential carbon–carbon coupling step at the Group 4 metallocene based homogeneous Ziegler–Natta catalyst systems [36,37].

There is a high current interest in the development of metallocene catalysts for the selective polymerization of functionalized olefins. Methylmethacrylate polymerization has been achieved with  $[\text{Cp}_2\text{SmH}]_2$  [38] but recently also with a small number of homogeneous catalysts based on zirconocene systems. The work described, e.g., by Collins [39], Soga [40], Höcker [41], and Gibson and coworkers [42] has shown that PMMA formation is highly dependent on the method of catalyst activation used.

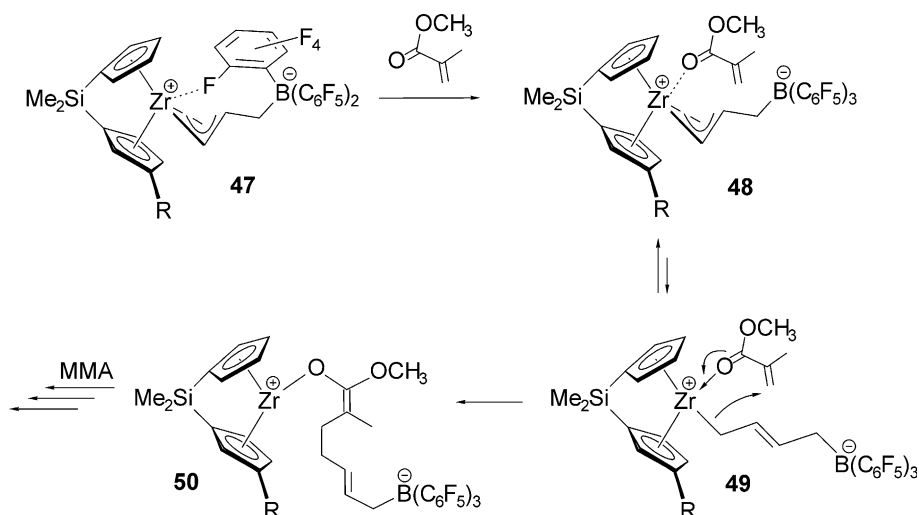
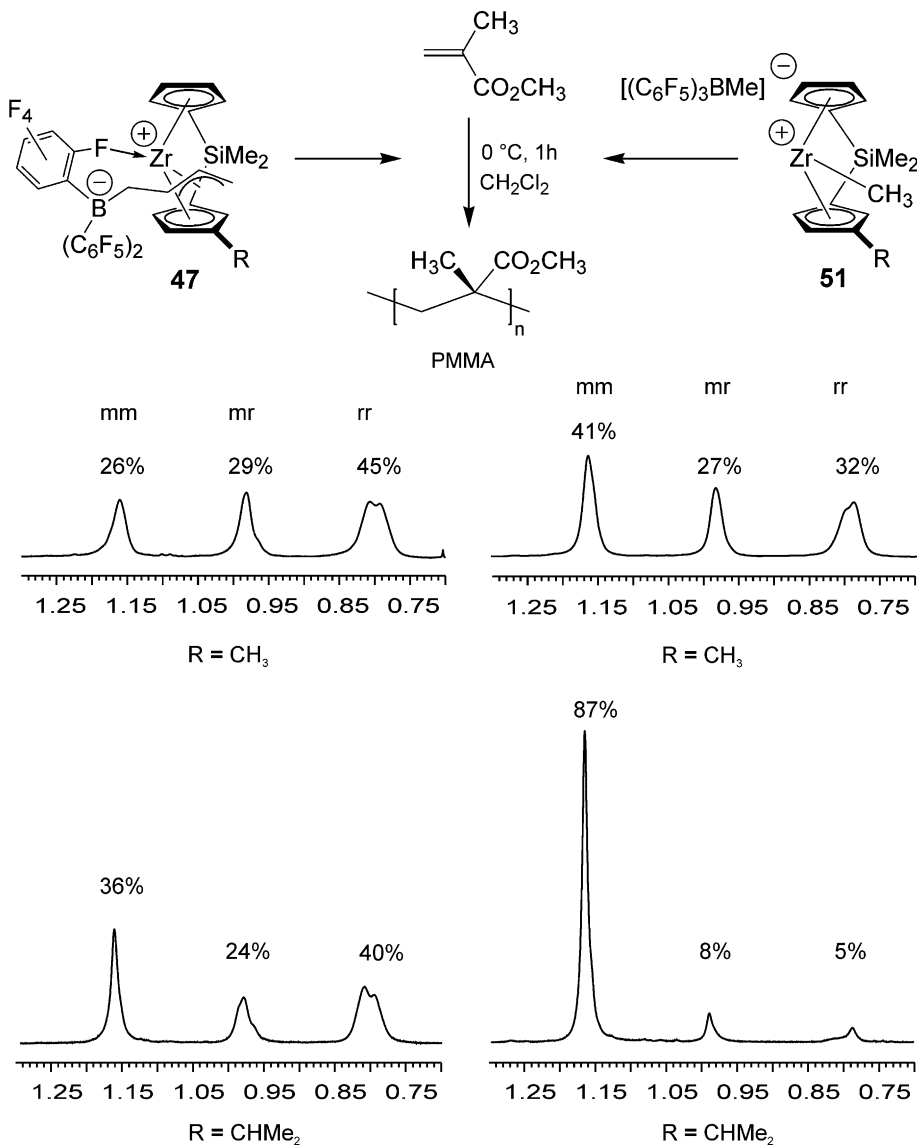
For our study [43] we have prepared a series of chiral  $\text{Me}_2\text{Si}$ -bridged *ansa*-zirconocene complexes and activated them by treatment with  $\text{B}(\text{C}_6\text{F}_5)_3$ . For his purpose we reacted the corresponding zirconocene dichlorides **44** with methyl lithium to form **45** and with “butadiene–magnesium” to yield mixtures of the respective (*s-cis*-) and (*s-trans*-butadiene)zirconocenes **46** (see Scheme 19).

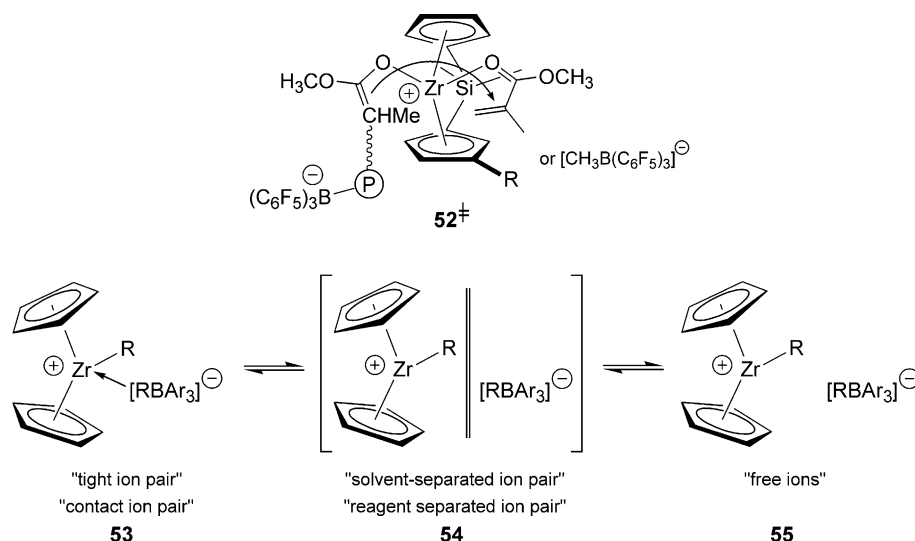
Addition of  $\text{B}(\text{C}_6\text{F}_5)_3$  to the isomer mixtures of the (butadiene) *ansa*-zirconocenes **46** in each case gave predominantly one diastereoisomer of the respective beta-tine system **47**. It reacted with methylmethacrylate (MMA) by formation of a Lewis acid adduct (**48**). Subsequently, the reaction sequence of PMMA formation was initiated by a Michael addition reaction of the  $\text{C}_4\text{H}_6\text{-B}(\text{C}_6\text{F}_5)_3$  ligand to yield a chain carrying zirconocene-enolate. Its repetitive addition to incoming MMA then led to the growth of the PMMA chain (see Scheme 20).

This mechanistic description is supported by the actual observation of an example of the initial MMA adduct (**48**) by low temperature NMR spectroscopy. In addition, quenching of a polymerization reaction mixture gave a series of the oligomeric  $\text{PMMA-C}_4\text{H}_6\text{-B}(\text{C}_6\text{F}_5)_3^-$



Scheme 19. Synthesis of chiral (butadiene)*ansa*-zirconocene complexes used as precursors for the generation of active homogeneous Ziegler–Natta catalyst systems for PMMA formation.

Scheme 20. Proposed reaction sequence leading to PMMA chain growth at the *ansa*-zirconocene(butadiene)/ $B(C_6F_5)_3$  betaine catalysts 47.Scheme 21.  $^1H$  NMR methyl triad signals of PMMA samples obtained at two pairs of 47/51 catalysts showing the different stereochemical outcome depending on the counteranion.



Scheme 22. Composition of some catalyst systems that may potentially involved in stereoselective PMMA formation at the single component metallocene catalysts.

anions that could be identified by electrospray-mass spectrometry.

The isotacticity of the polymethylmethacrylates obtained from the catalysts **47** critically depended on the steric bulk of the R-group attached at the *ansa*-metallocene framework. With R = *tert*-butyl a PMMA was obtained that showed a ca. 70% intensity of the  $^1\text{H}$  NMR methyl mm triad resonance. Isotactic PMMA was also obtained from the catalysts (**51**) that were obtained by  $\text{CH}_3^-$ -anion abstraction from the respective dimethylzirconocenes (**45**) by  $\text{B}(\text{C}_6\text{F}_5)_3$  (see Scheme 21). However, the catalyst systems **47** and **51** were found to differ substantially from each other. PMMA was formed with different catalyst activities, it featured different molecular weights and, most importantly, was quite different with regard to its stereoselectivity. In Scheme 21 this is visualized by the  $^1\text{H}$  NMR methyl triad resonances of PMMA samples obtained at two respective pairs of catalysts **47** and **51**, each bearing the same substituent R at the bent metallocene framework.

It is likely that the stereochemical outcome of the repetitive Zr-enolate addition to the coordinated methylmethacrylate monomer takes place in a rigid eight-membered ring transition state (**52<sup>‡</sup>**), similar as it is schematically depicted in Scheme 22. In this situation the differentiation between re- or si-side attack on the prochiral functionalized olefin is primarily determined by the bulk of the controlling R-group at the bent metallocene framework, but to some extent it seems also to depend on the nature of the counteranion that is involved. Since “contact ion pairs” (**53**) in this case are probably catalytically inactive and free ions (**55**) would not explain satisfactorily some of the experimental observations, we must probably assume that additional

types of ion pairs (**54**) are here involved, similarly as it has increasingly been discussed for related propene polymerization reactions catalyzed by homogeneous metallocene cation systems [44].

## 5. Some conclusions

(Butadiene)zirconocene was the first system for which the occurrence of the hitherto unobserved (*s-trans*- $\eta^4$ -conjugated diene)-coordination to a single transition metal center could be detected. Meanwhile the specific bonding features have been elucidated that may favour this specific coordination mode, and many additional examples have been found and described that favour this ligand geometry at a variety of metal complex frameworks.

The (butadiene)zirconocene systems have become interesting reagents in organic and organometallic chemistry and valuable starting materials for the generation of very active homogeneous catalysts for very fast and very selective carbon–carbon coupling reactions. The development of their chemistry will continue to help us in gaining additional fundamental as well as detailed insight into the features of such important reagent and catalyst types.

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