Direct Experimental Observation of the Stereochemistry of the First Propene Insertion Step at an Active Homogeneous Single-Component Metallocene Ziegler Catalyst

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Received October 13, 1998

Abstract: rac-[Me$_2$Si(1-indenyl)$_2$]ZrCl$_2$ was treated with (butadiene)magnesium to yield the respective ansa-metallocene (s-cis-η^4-butadiene) complex, **6**. It reacts with the organometallic Lewis acid B(C$_6$F$_5$)$_3$ to give the ansa-metallocene-(μ-C$_4$H$_6$)-B(C$_6$F$_5$)$_3$ betaine **7** that was characterized by X-ray diffraction. Complex **7** contains a distorted (σ,π-type) allyl ligand, bonded to zirconium, that bears a syn-oriented $-$CH$_2$B(C$_6$F$_5$)$_3$ substituent. An ortho C$-$F substituent of one of the C$_6$F$_5$ groups at boron coordinates to the electron-deficient zirconium center. Complex **7** is an active single-component Ziegler catalyst that stereoselectively polymerizes propene to give isotactic polypropylene by enantiomorphic site control (up to ca. 90% mmmm). Treatment of **7** with propene at -15 °C in toluene-d_8 leads to a regioselective but stereounselective stoichiometric monoinsertion of the prochiral 1-alkene into the Zr$-$CH$_2$ bond of the betaine **7** to give a 60:40 mixture of the metallacyclic products **9A** and **9B**. Cleavage of both the intramolecular C4$-$C5 olefin coordination to zirconium and the internal C6···Zr ion pair interaction in the **9A/9B** pair of diastereoisomers by the addition of THF yields a 60:40 mixture of the respective open-chain THF adducts **10A** and **10B**. This result shows that the first propene insertion reaction at the rac-[Me$_2$Si(1-indenyl)$_2$]Zr derived single-component Ziegler catalyst system is not stereoselective, whereas all subsequent propene insertion steps show a high degree of stereoselectivity. A stereochemical "relay mechanism" is proposed to account for this behavior, where an intermediately generated stereogenic center at the α-carbon atom of the growing σ-ligand hydrocarbon chain effectively serves to transfer the stereochemical information from the chiral metallocene backbone onto the growing carbon chain. The ansa-metallocene backbone alone seems to have no intrinsic ability for direct stereochemical control. The essential role of the α-carbon stereochemistry is supported by the stereoselective propene insertion into the betaine (**16**) derived from the regioselective B(C$_6$F$_5$)$_3$ addition to (1,3-pentadiene)ZrCp$_2$.

Introduction

The chemistry of homogeneous single-metal-center Ziegler type catalysts based on the group 4 metals, especially on zirconium, has seen some interesting and rapidly expanding development recently.[1] One aspect, on which a considerable amount of attention has been focused, is the design of single-component catalyst systems.[2] These are molecular arrangements in which the catalytically active d-block metal center is connected to the essential activator component, usually comprised of an electrophilic group 13 element in a suitable σ-ligand environment, by a covalent linker in a single molecule. In metallocene-based chemistry, there have been a number of attempts to attach, e.g., $-$B(C$_6$F$_5$)$_n$ units as substituents at the Cp ligands.[3] A conceptually different approach has been to design single-component metallocene Ziegler catalyst systems (and their nonmetallocene analogues) where the Cp$_2$Zr$^+$ unit is connected with its X$^-$ counteranion by means of a covalently bonded insertion-active hydrocarbyl chain.[4,5] In this way, many

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Scheme 1
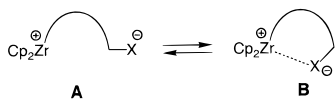
problems associated with the ubiquitous ion-pairing phenomenon of the conventional $Cp_2ZrR^+\cdots X^-$ catalyst species[6] can be circumvented and molecularly very well defined catalyst systems can easily be made that are based on this simple structural concept (see Scheme 1).

A prominent example of this type of very active homogeneous single-component Ziegler catalyst system is obtained by the addition of the strong organometallic Lewis acid tris(pentafluorophenyl)borane (**2**)[7] to (butadiene)zirconocene (**1**).[8] The addition takes place regioselectively to quantitatively yield the metallocene−(μ-conjugated diene)−borate betaine system **3**. A great variety of (conjugated diene)metallocenes (and related compounds) have been shown to undergo this type of electrophilic addition reaction.[5] In the case of the parent Cp_2Zr-(butadiene)/$B(C_6F_5)_3$ system, the resulting compound **3** contains a framework that exhibits a syn-configurated substituted distorted π-allyl ligand at zirconium.[9] Characteristically, complex **3** exhibits a single $Zr\cdots F-C$ interaction with one ortho-C_6F_5-fluorine atom.[5a,b,10] This weak interaction (the $Zr\cdots F-C$ bond dissociation energy is ca. 8 kcal mol^{-1})[5b] serves to protect the electrophilic zirconium center. It is opened reversibly, and a further π-allyl $\rightleftharpoons$ σ-allyl equilibration generates an active α-olefin polymerization catalyst species (see Scheme 2). A remarkable feature of the catalyst system **3** (and its congeners

derived from other metallocenes and related systems[11]) is that it allows for an experimental observation of the first 1-alkene insertion step in some detail, since the primary product **4** exhibits some internal coordinative/ion-pair stabilization.[12] Further insertion then rapidly leads to the formation of the respective polymer.

These unique features of the $^RCp_2Zr(butadiene)/B(C_6F_5)_3/$1-alkene reaction system have recently allowed for a first experimental characterization of the energy profile of the sequence of alkene addition/alkene insertion steps at an active metallocene Ziegler catalyst system.[13] At the specific system investigated (derived from the $(MeCp)_2Zr$ framework) it was found that alkene dissociation at the stage of the (π-alkene)-$ZrCp_2(R)$ intermediate appears to be slightly favored over alkene insertion by a factor of $k_{diss}/k_{ins} \approx$ 4:1 to 16:1 for the series ranging from propene to 1-hexene insertion.[14] Variants of the **3** → **4** type transformation should be ideally suited to characterize the stereochemistry of the insertion step. We have used the unique features of several $^RCp_2Zr(conjugated\ diene)/B(C_6F_5)_3/$propene systems to characterize the intrinsic ability of a metallocene framework to transfer its stereochemical information in the carbon−carbon coupling step onto a growing hydrocarbon chain. A set of representative examples is presented in this paper, and the results are compared with those obtained from actual polymerization experiments.

Results and Discussion

The stereochemical information of the rac-dimethylsilylene-bis(1-indenyl)zirconium ansa-metallocene backbone was utilized for this study. The corresponding rac-ansa-zirconocene dichloride starting material **5** was prepared and separated from its meso diastereomer as described in the literature.[15] rac-[Me$_2$Si(1-indenyl)$_2$]ZrCl$_2$ (**5**) was then treated with 1 molar equiv of the

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Scheme 2
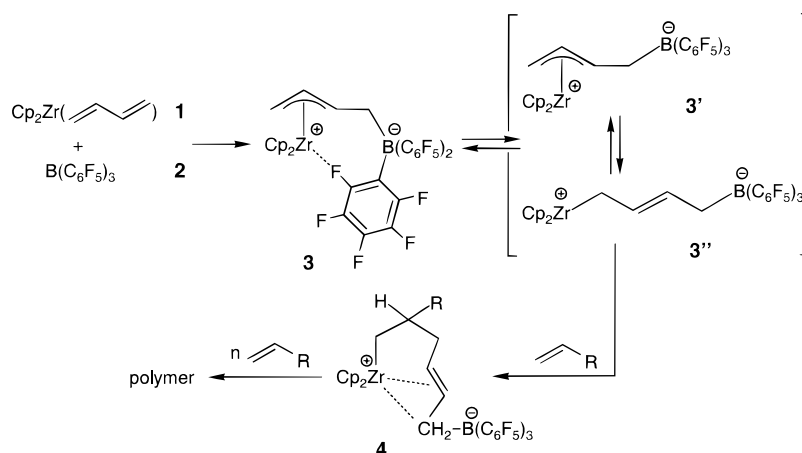
Scheme 3
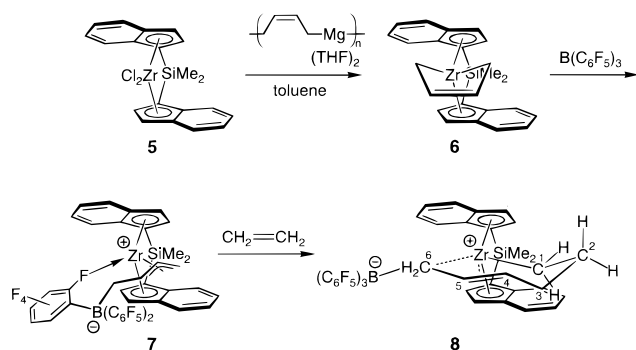
butadiene−magnesium reagent[16] to give the [Me$_2$Si(1-indenyl)$_2$]-Zr(butadiene) complex **6** (Scheme 3). Only a single isomer was detected. According to the characteristic NMR spectra[8] only the (s-cis-η^4-butadiene)Zr complex is present in solution. Due to the attachment to the chiral C$_2$-symmetric ansa-metallocene framework, the s-cis-butadiene ligand exhibits a set of four ^{13}C NMR resonances [δ 115.4, 114.0 (C3, C2); 59.3, 52.9 (C4, C1)]. At 253 K there are six C$_4$H$_6$ ^{1}H NMR resonances observed at δ −1.44, 2.28 (1-H$_{anti}$, 1-H$_{syn}$), −0.12, 2.41 (4-H$_{anti}$, 4-H$_{syn}$), and 3.67 and 4.41 (H-3, H-2). As a result of the envelope-shaped Zr(s-cis-butadiene) framework, the indenyl moieties are diastereotopic, and the metal chirality at the central zirconium atom results in the observation of a set of diastereotopic NMR signals of the Me$_2$Si methyl groups. Increasing the monitoring temperature brings the system into a situation where the topomerization[17] of the Zr(s-cis-butadiene) framework (the typical "ring flip" of the metallacyclic five-membered ring system) becomes rapid on the NMR time scale. A coalescence of the respective pairs of NMR signals is observed. From the equilibration of the methine C*H* signals of the indenyl moieties we have calculated a Gibbs activation energy of $\Delta G^{\ddagger}_{inv}$ (318 K) = 17.7 ± 0.3 kcal mol^{-1} for this ring-inversion process at the coalescence temperature. This is within a range typically observed for many (butadiene)zirconocene complexes, albeit being located at the high-energy end of the scale.[8b]

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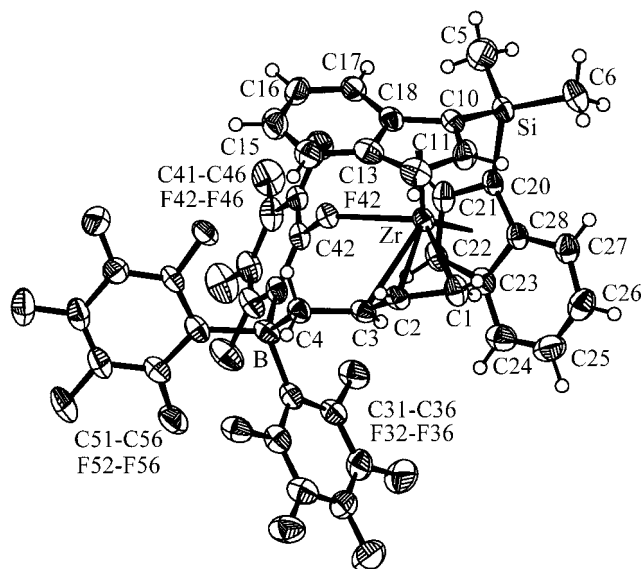
Figure 1. Molecular structure of the metallocene-borate-betaine complex **7**. Selected bond lengths (Å) and angles (deg): Zr−C1 2.343(7), Zr−C2 2.485(6), Zr−C3 2.635(6), Zr−C4 3.674(6), Zr−F42 2.483(3), F42−C42 1.393(7), Zr−C$_{Cp}$ 2.530(7), C1−C2 1.409(8), C2−C3 1.352(8), C3−C4 1.515(8), C4−B 1.636(10), B−C31 1.636(10), B−C41 1.653(10), B−C51 1.662(10), C10−Si 1.863(7), C20−Si 1.873-(7), Si−C5 1.856(8), Si−C6 1.854(8); Zr−F42−C42 138.0(3), C1−Zr−C2 33.8(2), C1−Zr−C3 58.4(2), C2−Zr−C3 30.5(2), Zr−C1−C2 78.6(4), Zr−C2−C1 67.6(3), Zr−C2−C3 80.9(4), Zr−C3−C2 68.7(3), C1−C2−C3 124.3(6), C2−C3−C4 124.7(6), C3−C4−B 116.1(5), C4−B−C31 103.3(6), C4−B−C41 114.3(5), C4−B−C51 110.3(5), C31−B−C41 113.7(6), C31−B−C51 113.9(6), C41−B−C51 101.8(6), C10−Si−C20 94.1(3), C10−Si−C5 115.3(4), C10−Si−C6 111.2(4), C20−Si−C5 109.9(4), C20−Si−C6 114.2(3), C5−Si−C6 111.2(4).

B(C$_6$F$_5$)$_3$ adds cleanly to [Me$_2$Si(indenyl)$_2$]Zr(s-cis-η^4-butadiene), **6**, to yield the ansa-metallocene−(μ-C$_4$H$_6$)−borate betaine system, **7**. Single crystals of the 1:1 addition product were obtained from toluene solution. The X-ray crystal structure analysis (see Figures 1 and 2) shows that the borane reagent was added to a −CH$_2$ terminus of the conjugated diene ligand. A new carbon-to-boron single bond was formed (d C4−B 1.636-(10) Å). Carbon atom C4 is sp^3 hybridized (angle C3−C4−B 116.1(5)°), and it is no longer connected to zirconium (Zr···C4 separation: 3.674(6) Å). The three remaining former butadiene carbon atoms form a monosubstituted distorted η^3-allyl ligand at zirconium.[5,8,18] The Zr−C1 bond is rather short, at 2.343(7) Å.[19] The Zr−C2 (2.485(6) Å) and Zr−C3 (2.635(6) Å) linkages
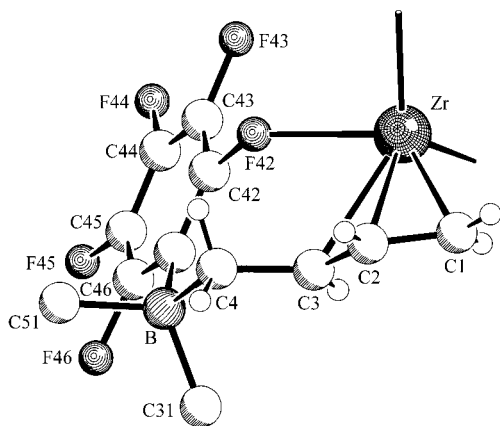
Figure 2. View of the central core of atoms of the structure of **7**.

are increasingly longer. The corresponding carbon−carbon distances amount to 1.409(8) Å (C1−C2), 1.352(8) Å (C2−C3), and 1.515(8) Å (C3−C4). The C1−C2−C3 and C2−C3−C4 angles inside the (π-allyl)metallocene unit are 124.3(6)° and 124.7(6)°, respectively.

The allyl ligand in **7** is syn-substituted;[20] i.e., it exhibits *E* configuration at the central C2−C3 π-bond of the C1−C4 framework. This brings one of the C_6F_5 substituents at boron into close vicinity of the electrophilic zirconium center. Consequently, the fluorine atom of the C42−F42 ortho C−F bond at this pentafluorophenyl group coordinates to zirconium (C42−F42: 1.393(7) Å, Zr−F42: 2.483(3) Å, angle C42−F42−Zr 138.0(3)°). Analogous pronounced C−F···Zr interactions have previously been observed at other related group 4 metallocene−(μ-conjugated diene)−borate betaine systems.[5a,b] Fluorine coordination from a C−F bond to zirconium seems to provide a suited stabilization of the metallocene cation end in such a dipolar betaine structural situation, provided that suitable geometric parameters can be obtained.[5c,18] The ansa-metallocene framework in **7** shows the expected typical structural features. Figure 1 shows a view of the molecular structure of **7** in the crystal. Figure 2 provides a projection of the central core of atoms of **7**.

The C−F to zirconium coordination in **7** probably persists in solution, like in the analogously structured $^RCp_2Zr$(butadiene)/$B(C_6F_5)_3$ addition products that we have studied and structurally characterized previously.[5] However, due to the rapid dynamic exchange only a set of three (i.e., ortho, meta, and para) aryl−CF ^{19}F NMR resonances are observed for **7** at ambient temperature. The ^{13}C NMR spectrum of **7** shows resonances of the distorted (i.e., σ,π-bonded) allyl moiety at δ 67.9 (C1), 136.5 (C2), and 121.8 (C3), whereas the signal of carbon atom C4, that is bonded to boron, appears at ca. 24 ppm. As expected, the six hydrogen atoms at the allyl−CH_2−[B] unit are all differentiated, and the two indenyl residues are diastereotopic, as are the methyl substituents at the bridging silicon atom.

Complex **7** is an active one-component Ziegler catalyst for the polymerization of ethene and α-olefins. It rapidly polymerizes ethene at 40 °C to give polyethylene (mp 134 °C) with an activity of >2000 g of polyethylene/mmol [Zr]·bar·h. Propene is also rapidly polymerized to give isotactic polypropylene (T_{polym} = 40 °C, p(propene) = 2 bar, $a \approx 1200$ g of

polypropylene/mmol [Zr]·bar·h, [mmmm] = 77%; p(propene) = 1 bar, $a \approx 1100$, [mmmm] = 81%; p(propene) = 0.5 bar, a = 830, [mmmm] = 91%). For further details see the Experimental Section.

When ca. 3 mL of gaseous ethene was slowly passed through a solution of **7** in toluene-d_8 at −20 °C and the mixture was then kept for several hours at −15 °C, ca. 70% of the starting material was consumed and selectively converted to the monoinsertion product **8**. Complex **8** was by far too sensitive and reactive to be isolated, but it was sufficiently characterized by ^{1}H/^{13}C NMR spectroscopy. The assignments were secured by 1D-TOCSY, GCOSY, GHSQC, and GHMBC experiments[21] using a 600/150 MHz NMR spectrometer. The ethene-insertion reaction has resulted in the formation of a six-carbon chain connecting zirconium and boron in complex **8**. Methylene carbon atoms C1−C3 show resonances at δ 67.8, 38.1, and 35.0. The C4 and C5 resonances occur at δ 141.9 and 134.2 which strongly indicates a coordinative interaction of the C4=C5 double bond with the electrophilic zirconium center (secured by a comparison with the respective chemical-shift values of the parent compound, **4**; see above and suitable reference systems[12,22]). The C6 resonance was located at ca. δ 14 ppm, which indicates some internal ion-pair interaction with the Zr metal center.[12] As expected for this structural type (see Schemes 3 and 2), the CH_2 hydrogens at the [Zr]−$CH_2CH_2CH_2$-CH=CHCH$_2$−[B] chain are pairwise diastereotopic, as are the indenyl residues of the ansa-metallocene backbone and the methyl groups at the bridging silicon. The diastereotopism of these respective groups at the Me_2Si(indenyl)$_2$ framework indicates metal chirality in **8**, which conditionally requires an unsymmetrical coordination of the C_6-ligand chain at the front side of the bent metallocene wedge.

Actually, the product **8** contains two independent elements of chirality, namely the chiral [Me_2Si(1-indenyl)$_2$]Zr backbone and the element of planar chirality that is introduced by intramolecular coordination of the unsymmetrically substituted internal (trans)C=C double bond of the C_6 chain to the zirconium center. Thus, there should be the possibility that principally two diastereoisomeric mono-ethene-insertion products might be formed (**8** and **8′**) that would differ in their combination of the relative configurations of their pairs of chirality elements. If we designate the reference configuration of the [Me_2Si(1-indenyl)$_2$]Zr backbone as "ansa-*R**", then the two possible diastereoisomers would be characterized by relative configurations ansa-*R**,4,5,6-p-*R** and ansa-*R**,4,5,6-p-*S**, respectively. Obviously, one of these diastereomeric arrangements is much preferred over the other, since we have only observed a single diastereoisomeric product to be formed upon treatment of the betaine **7** with ethene at low temperature. Which of the two diastereoisomeric possibilities this is, we do not know; but we must conclude that the chiral ansa-metallocene backbone strongly controls which one of the two modes of internal alkene coordination to zirconium inside the resulting seven-membered metallacyclic of the product **8** becomes by far preferred.

Complex **7** was treated in the same way with propene in toluene-d_8 at low temperature (ca. −15 °C) to yield the respective monoinsertion products. Insertion takes place regioselectively[12] to give the C_6 chain bearing the newly introduced

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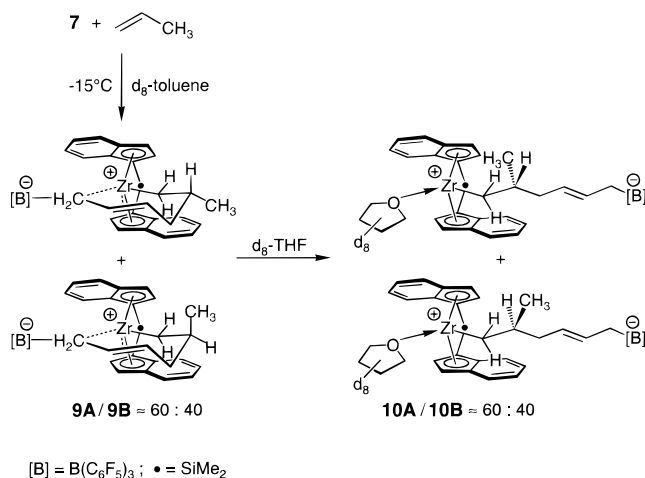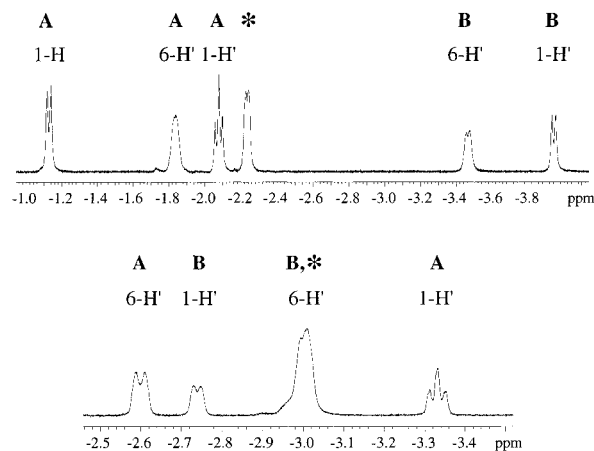
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Scheme 4

Figure 3. ^{1}H NMR 1-H/H′ and 6-H/H′ resonances of the **9A/B** (top, in toluene-d_8) and **10A/B** mixture (bottom, in toluene-d_8/THF-d_8); the asterisk marks the 1-H resonance of residual **7** or **7·THF** starting material.

methyl group at the β-position to the transition metal. In this case coupling of the prochiral 1-alkene with the CH_2 terminus of the C_4-ligand chain of the metallocene−(μ-C_4H_6)−borate betaine reagent generates a chiral center at carbon atom C2 in addition to the element of planar chirality and the given chirality of the ansa-metallocene backbone. This might lead to the formation of a total of four diastereomeric insertion products of relative configurations ansa-*R**,2-*R**,4,5,6-p*R**, ansa-*R**,2-*R**,4,5,6-p*S**, ansa-*R**,2-*S**,4,5,6-p*R**, and ansa-*R**,2-*S**,4,5,6-p*S**, respectively. However, the insertion reaction of propene into the Zr−C bond of **7** shows some stereoselectivity. At −15 °C the reaction proceeds smoothly to give a mixture of only two diastereoisomers, **9A** and **9B**, that were formed in a ca. 60:40 ratio (Scheme 4). Both complexes exhibit distinctively different ^{1}H and ^{13}C NMR spectra, but are of a very similar overall appearance. Both are of the same regioisomeric-insertion type and, thus, exhibit the propene derived methyl substituent at carbon atom C2 of the newly formed C_6 chain. According to the detailed NMR analysis (for details see the Experimental Section and the Supporting Material) both show internal coordination of the C4=C5 double bond to zirconium, and for both, one must assume an internal ion-pair interaction between the metallocene and the negatively polarized C^6H_2-[B] carbon end of the C_6 chain.[12,18,23] Thus, we must conclude that the two obtained isomers are distinguished by their combination of the relative configurations of the pairs of newly formed chirality elements. A likely scenario would be that either the element of planar chirality is formed unselectively or that the C2 chirality center, whose stereochemistry is established in the CC-coupling step during the insertion process, is formed unselectively. A priori, we cannot distinguish beyond doubt between these two possibilities, although our previous observation that the **7** plus ethene insertion reaction yields only a single diastereoisomer might let us favor the latter of the two alternatives. This would indicate that the initial propene insertion into the Zr−C bond at the [Me_2Si(1-indenyl)$_2$]Zr-derived catalyst system proceeds without a significant stereocontrol. We considered it necessary to secure this finding beyond doubt experimentally. This was possible by carrying out a subsequent reaction of **9** that led to decomplexation of the internal C4=C5 alkene and removal of the zirconium to C6 ion-pair coordination. This was readily achieved by treatment of the **9A/9B** mixture with tetrahydrofuran. Addition of a sufficient quantity of THF-d_8 to a **9A/9B** solution in toluene-d_8 proceeded cleanly and gave the corre-

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sponding THF addition products. A mixture of two complexes, **10A** and **10B**, is obtained. These are formed in the same ratio in which **9A** and **9B** were originally present in the solution, namely ca. 60:40.

The very characteristic changes of the NMR spectra shall be illustrated for the example of several typical ^{13}C NMR signals of the complexes **9A/B** and **10A/B**. The C1 resonances of **9A** and **9B** are observed at δ 77.0 and 67.0, respectively. Addition of THF leads to a characteristic shifting of these resonances to smaller δ values (**10A**: C1 at δ 54.3, **10B**: 44.9 ppm). The coordinated C4=C5 double bond shows ^{13}C NMR resonances at δ 138.9 and 133.9 in **9A**. These shift to δ 118.8 (C4) and δ 119.8 (C5) upon formation of **10A**. Finally, the ^{13}C NMR chemical shift of the C6 methylene group signals (C^6H_2-[B]) in **9A/9B** are at typical values of ca. δ 14 ppm, indicating the presence of an internal Zr···C^6H_2-[B] ion-pair interaction. These chemical shift values change drastically when the internal ion pair is cleaved by the addition of THF (C6 resonance of **10A**: δ 49.1, **10B**: δ 52.3 ppm). Similarly pronounced ^{1}H NMR effects are associated with the **9A/B** → **10A/B** transformation. The view Figure 3 provides of the 1-H/H′ and 6-H/H′ ^{1}H NMR resonances of the **9A/B** and **10A/B** pairs makes the resonances easily recognized by their extreme upfield positions in the spectra.

The observation of identical 60:40 **9A/9B** and **10A/10B** ratios before and after the addition of THF clearly indicates that the first propene insertion at the [Me_2Si(1-indenyl)$_2$]Zr derived catalyst system **7** is almost completely stereo nonselective. The C_2-symmetric chiral rac-[Me_2Si(1-indenyl)$_2$]Zr framework does not at all transfer its stereochemical information onto the growing hydrocarbon chain in the course of the very first insertion step, although it is very well suited to carry out a high stereocontrol very effectively in the second and each of the following steps as is apparent from the overall stereoselective propene polymerization catalysis observed in toto at **7** and at related catalysts derived from the [Me_2Si(1-indenyl)$_2$]Zr system by using other methods of catalyst activation.[15] A specific result of our study, thus, is that the [Me_2Si(1-indenyl)$_2$]Zr derived catalyst system **7** is acting nonselectively in only the first step of the propene polymerization reaction sequence under our typical reaction conditions. Thus, the rac-[Me_2Si(1-indenyl)$_2$]-Zr framework appears not to have an intrinsic potential to successfully transfer its stereochemical information in an olefin CC-coupling reaction without suited special assistance from other parts of the complex polymerization catalyst system. In

Scheme 5
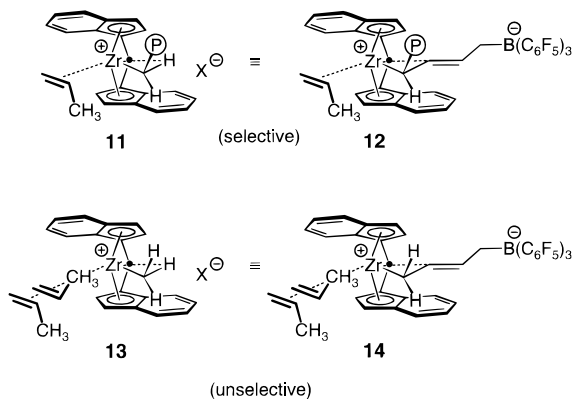
other words, it needs a *chemical relay* for effectively transferring its stereochemical properties.

A similar observation in the high pressure propene polymerization regime was recently made by the groups of Sacchi and Brintzinger,[24] using a variation of a method earlier applied by Zambelli et al.[25] They carried out a propene-polymerization reaction starting with the specifically ^{13}C-labeled rac-[Me$_2$Si-(1-indenyl)$_2$]Zr-[13]CH$_3$[+] cation complex and measured the ratio of $-CH_2-CHMe-CH_2-CHMe($[13]CH_3) erythro and threo end groups of the isolated polymer samples. This ratio serves as a measure of the stereoselectivity of the very first propene insertion step at this catalyst system under the specific reaction conditions chosen. Under typical polymerization conditions the rac-[Me$_2$Si(1-indenyl)$_2$]Zr-[13]CH$_3$[+] derived catalyst system gave polypropylene with a reasonably high isotacticity (mmmm pentade intensity $\geq$ 70%), but the erythro/threo end-group ratio was ca. 60:40, which is identical to our independently obtained value (see above). The rac-[Me$_2$Si(1-indenyl)$_2$]Zr backbone apparently exerts no significant stereocontrol in the first propene insertion step of the CH$_2$=CHCH$_3$ polymerization process under these conditions. Its intrinsic ability to directly control the Re/Si ratio of the incoming olefin or an Re/Si preference in the actual CC coupling step must probably be regarded as negligible.

The difference in stereochemical performance of these catalysts between the first and all subsequent propene insertion steps probably indicates a stereochemical relay mechanism that is in operation at these systems.[26] It is likely that an α-agostic interaction[27,28] is built up in the essential transition state or reactive intermediate of the repetitive insertion step of the polymerization reaction (**11** in Scheme 5). It seems that it is the stereochemistry of the newly formed stereogenic carbon center in **11** that is effectively controlled by the ansa-metallocene framework and that this stereocenter at the α-carbon of the

growing σ-ligand chain, then, very effectively controls the stereochemically preferred incorporation of the added prochiral α-olefin.[29] In view of the Curtin−Hammett behavior of such catalyst systems, at least in the low pressure regime as recently shown by us for a representative example,[13] the "relay stereocontrol" is most likely to occur in the actual insertion transition state (favoring the propene CH$_3$ group and the polymer chain P (see Scheme 5) in a trans arrangement) rather than in the olefin precoordination step. In the very first insertion step starting either from rac-[Me$_2$Si(1-indenyl)$_2$]Zr-[13]CH$_3$[+] or rac-[Me$_2$Si(1-indenyl)$_2$]Zr[+]CH$_2$CH=CHCH$_2$B(C$_6$F$_5$)$_3$[−] neither the α-CH agostic (in **13**) nor the related α−π-agostic[4a] interaction (in **14**) creates a new stereogenic center, and thus the relay that is necessary for stereocontrol is lacking, and the first propene insertion consequently takes place stereochemically uncontrolled.

Our metallocene−betaine approach has allowed us to design and generate a suitable model system for this stereochemical "relay effect" in a very simple way. The influence of the growing chain at the α-carbon atom can, in principle, already be mimicked by attaching a methyl group at the carbon end of the C$_4$ chain in the zirconocene−(μ-conjugated diene)−borate betaine catalyst system. Stereochemical control analogously as described above should then result in a large preference of the respective trans-disubstituted CC-coupling product upon insertion of a propene molecule. We were able to observe this effect at the following suitably substituted system.

Treatment of zirconocene dichloride with lithium sand in ether in the presence of 1,3-pentadiene gave a 1:1 mixture of (s-cis-) and (s-trans-η^4-1,3-pentadiene)zirconocene (**15**).[8b,30] The addition of B(C$_6$F$_5$)$_3$ took place regioselectively at the less hindered, unsubstituted =CH$_2$ end of the conjugated diene ligand to give the methyl-substituted zirconocene−(μ-diene)−borate betaine system **16**. This shows ^{1}H NMR Cp singlets at δ 5.26 and 5.20. Both the methyl substituent at C1 and the C^{4}H$_2$-[B] unit are syn-arranged (relative to 2-H) at the η^3-allyl moiety. The corresponding ^{1}H NMR signals are observed at δ 2.43 (1-H anti), 5.53 (2-H), 4.39 (3-H anti), and 2.20 and 1.54 (4-H/H′).

The propene insertion into **16** was carried out at −15 °C in toluene-d_8 analogous to that for **7** as described above. The CC-coupling reaction under these conditions is strictly stoichiometric and pauses after the first insertion step. The reaction is highly regioselective. Coupling only occurs at the methyl-substituted end of the allyl unit of the betaine reagent, and the propene methyl group ends up in the β-position (C2 of the product **18**, see Scheme 6) relative to the zirconium metal of the resulting C$_6$-product chain. The coupling reaction is completely stereoselective within the limits of ^{1}H NMR detection. A single stereoisomer is formed. Again this shows a pair of diastereotopic Cp ligands (^{1}H NMR signals at δ 5.31 and 5.08) and pairwise diastereotopic protons at C1 (1-H/H′: δ 0.95, −0.64) and C6 (6-H/H′: δ 1.15, −0.48 ppm). The C4=C5 double bond is likely to be coordinated to zirconium (^{13}C NMR resonances at δ 143.6 (C4) and 122.8 ppm (C5)).[12,22] From the spectroscopic data we assume that the methyl substituents of **18** at carbon atoms C2 and C3 are trans-oriented at the framework (2-R^*,3-R^*-diastereoisomer). This is evident from coupling constants $^3J_{1-H(ax),2-H} = 12.8$ Hz, $^3J_{1-H(eq),2-H} = 1.9$ Hz, $^3J_{2-H,3-H} \approx 10$ Hz, and $^3J_{3-H,4-H} = 10$ Hz. There is a strong NOE response between 2-H and 4-H.

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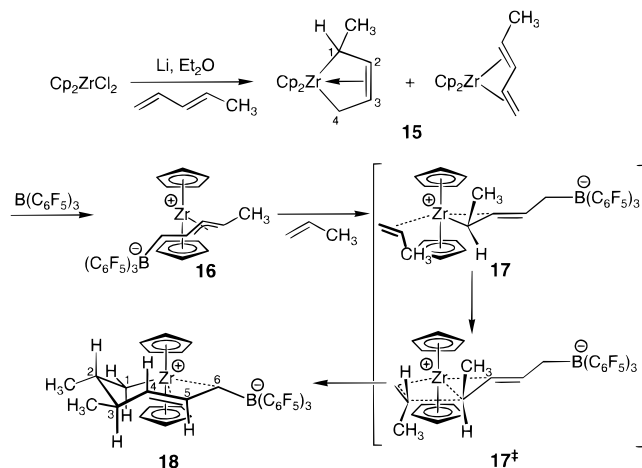
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Scheme 6

This result indicates the importance of the substitution pattern at the α carbon of the σ-ligand chain for the stereocontrol of the insertion of a prochiral 1-alkene. The stereochemistry of the CC-coupling process seems to be controlled very effectively by the relative arrangement of the substituent at the α-carbon atom of the migrating chain and the 1-alkene substituent. In the insertion transition state ($17^{‡}$) these, necessarily, come very close together. Steric control in the insertion transition state seems to govern the insertion stereochemistry, favoring a trans arrangement whenever possible.

Conclusions

This study has provided independent experimental evidence[24] that stereocontrol of the chiral-metallocene backbone of the rac-[Me$_2$Si(1-indenyl)$_2$]Zr system, which is a typical example for a whole class of compounds, in diastereoselective 1-alkene coupling and polymerization is not proceeding by a direct interaction between the ansa-metallocene framework and the incoming alkene but rather takes place by means of a relay mechanism involving and utilizing the α-carbon atom of the growing σ-alkyl chain for transporting of the stereochemical information. In the actual polymerization process this is most likely effected by the presence of an α-agostic C−H···Zr interaction that introduces a new intermediate chiral center at C$^{\alpha}$, thus leading to diastereomeric differentiation in the insertion transition state. In our betaine model system it is likely that a π-agostic interaction is effectively mimicking this situation, which analogously results in the generation of a chirality center at C1. Its preferred configuration seems to be controlled by the chiral bent-metallocene backbone, and it is the C1 stereogenic center that then, in turn, controls the stereochemistry of the actual insertion process by steric interaction between its substituents and the substituents at carbon atom C2 of the inserting α-olefin. It seems that the characteristics of the alkene-addition/insertion energy profile, as it was experimentally determined by us recently for a first example,[13] may require this rather complicated mode of transfer of the stereochemical information from the ansa-metallocene backbone through the α-carbon of the growing chain onto the CC-coupled product. It may be that many ansa metallocenes, which are effective and typically employed in stereoselective α-olefin polymerization, contain backbones that are ineffective for a direct transfer of their stereochemical information and may require such a stereochemical caskade. Our metallocene−(conjugated diene)−borate betaine systems seem to be well-suited model systems to investigate a great variety of different backbones for their

intrinsic stereochemical control abilities. It may be that in this way metallocene backbones could be detected and assigned that are capable of a direct stereochemical direction of incoming prochiral alkenes, a feature that would make them useful candidates for potential future applications of such highly reactive, selective metallocene catalysts for CC-coupling processes in asymmetric organic synthesis.[31] We have begun to carry out such studies in our laboratory.

Experimental Section

General Remarks. All manipulations involving air-sensitive compounds were carried out under argon in a glovebox or using Schlenk type glassware. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. Zirconocene dichloride, rac-[dimethylsilylenebis(1-indenyl)]dichlorozirconium,[15] "butadiene−magnesium",[16] and tris(pentafluorophenyl)borane[7] were prepared according to literature procedures. Caution is advised in the preparation of B(C$_6$F$_5$)$_3$, since the LiC$_6$F$_5$ intermediate is potentially explosive if brought to temperatures that are too high. NMR experiments were performed on a Varian Unity Plus 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F: 564 MHz). Assignments in ^{1}H and ^{13}C NMR spectra were confirmed by GCOSY, 1D-TOCSY, GHSQC, and GHMBC spectra.[21] IR spectra were aquired on a Nicolet 5 DXC Fourier transform IR spectrometer. Melting points were obtained by differential scanning calorimetry (DuPont 910) and elemental analyses were determined on a Foss−Heraeus CHN-Rapid elemental analyzer.

rac-[Dimethylsilylenebis(1-indenyl)](s-cis-η^4-butadiene)zirconium (6). To a mixture of rac-[dimethylsilylenebis(1-indenyl)]dichlorozirconium (1.85 g, 4.13 mmol) and butadiene−magnesium (1.02 g, 4.57 mmol) was slowly added toluene (80 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h. The precipitate of magnesium chloride was filtered off, and the solvent was removed from the filtrate in vacuo. Recrystallization of the crude product from toluene at −20 °C afforded the red butadiene complex **6**, which was isolated by filtration, washed twice with pentane (15 mL), and dried in vacuo. Yield: 921 mg (52%). Mp: 203 °C. ^{1}H NMR (toluene-d_8, 599.9 MHz, 253 K): δ = 7.77 (d, ^3J = 8.5 Hz, 1H, Ind-Ar), 7.63 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H, Ind-Ar), 7.39 (d, ^3J = 8.5 Hz, 1H, Ind-Ar), 6.86 (ddd, ^3J = 8.5 Hz, ^3J = 6.3 Hz, ^4J = 1.0 Hz, 1H, Ind-Ar), 6.80 (ddd, ^3J = 8.5 Hz, ^3J = 6.6 Hz, ^4J = 1.0 Hz, 1H, Ind-Ar), 6.67 (m, 3H, Ind-Ar), 6.35 (d, ^3J = 3.1 Hz, 1H, Ind-Cp), 5.80 (d, ^3J = 3.3 Hz, 1H, Ind-Cp), 5.25 (d, ^3J = 3.1 Hz, 1H, Ind-Cp), 5.15 (d, ^3J = 3.3 Hz, 1H, Ind-Cp), 4.41 (m, 1H, butadiene internal H), 3.67 (m, 1H, butadiene internal H), 2.41 (dd, ^2J = 9.5 Hz, ^3J = 9.5 Hz, 1H, butadiene terminal H), 2.28 (dd, ^2J = 9.5 Hz, ^3J = 9.5 Hz, 1H, butadiene terminal H), 0.76, 0.70 (each s, 3H, Si(CH$_3$)$_2$), −0.12 (ddd, ^2J = 9.5 Hz, ^3J = 12.0 Hz, ^4J = 1.2 Hz, 1H, butadiene terminal H), −1.44 (dd, ^2J = 9.5 Hz, ^3J = 11.8 Hz, 1H, butadiene terminal H) ppm. ^{13}C NMR (toluene-d_8, 150.8 MHz, 253 K): δ = 126.8 (CH, Ind-Ar−CH), 126.3 (C, Ind-C), 126.1 (CH, Ind-Ar−CH), 125.8 (C, Ind-C), 125.2 (under solvent signal), 125.0, 124.8 (each CH, Ind-Ar−CH), 123.3 (C, Ind-C), 122.7, 122.1 (each CH, Ind-Ar−CH), 122.0 (C, Ind-C), 120.8 (CH, Ind-Ar−CH), 115.4, 114.0 (each CH, butadiene-*C*H), 111.6, 107.0, 105.9, 102.8 (each CH, Ind-Cp-CH), 92.5 (C, Ind-ipso-C), 86.6 (C, Ind-ipso C), 59.3, 52.8 (each CH$_2$, butadiene-*C*H$_2$), −1.4, −1.8 (each CH$_3$, Si(*C*H$_3$)$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2962, 1447, 1306, 1259, 1251, 1142, 1133, 965, 830, 811, 802, 781, 751, 742, 683 cm^{-1}. Anal. Calcd for C$_{24}$H$_{24}$SiZr: (431.8): C, 66.76; H, 5.60. Found: C, 65.16; H, 5.85.

Formation of the Metallocene−(μ-Butadiene)−Borate Betaine Complex 7. A solution of the betaine **7** may be generated in situ by the addition of a solution of the butadiene zirconium complex **6** (16.2 mg, 37.5 μmol) in 2 mL of toluene-d_8 to a solution of tris(pentafluorophenyl)borane (19.2 mg, 37.5 μmol) in 1 mL of toluene-d_8. Betaine **7** was isolated on a preparative scale by adding a solution of complex **6** (100 mg, 0.23 mmol) in toluene (3 mL) to a solution of tris(pentafluorophenyl)borane (130 mg, 0.25 mmol) in toluene (2 mL).

(31) Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 4715. Thiele, S.; Erker, G. *Chem. Ber.* **1997**, *130*, 201.

The reaction mixture was allowed to stand for 3 days at room temperature. During this time the betaine complex **7** precipitated from the solution as orange crystals, which were isolated by filtration, washed with pentane (4 mL), and dried in vacuo. Yield: 117 mg (54%). Mp 135 °C. ^{1}H NMR (toluene-d_8, 599.9 MHz, 253 K): $\delta = 7.27$, 7.20 (each d, $^3J = 8.6$ Hz, 1H, Ind-Ar), 7.07, 6.66, 6.43 (each m, 2H, Ind-Ar), 5.97 (d, $^3J = 3.1$ Hz, 2H, Ind-Cp), 5.80 (m, 1H, 2-H), 5.69, 4.27 (each d, $^3J = 3.1$ Hz, 1H, Ind-Cp), 4.17 (broad d, $^3J = 16.3$ Hz, 1H, 3-H), 2.11, 1.75 (each broad d, $^2J = 18.7$ Hz, 1H, 4-H, 4-H′), 0.96 (dd, $^2J = 5.0$ Hz, $^3J = 8.3$ Hz, 1H, 1-H), 0.44, 0.04 (each s, 3H, Si-(CH$_3$)$_2$), -2.23 (dd, $^2J = 5.0$ Hz, $^3J = 11.6$ Hz, 1H, 1-H′) ppm. ^{13}C NMR (toluene-d_8, 150.8 MHz, 253 K): $\delta = 148.9$ (d, $^1J_{CF} = 250$ Hz, o-B(C$_6$F$_5$)$_3$), 138.6 (d, $^1J_{CF} = 250$ Hz, m-B(C$_6$F$_5$)$_3$), 136.5 (CH, C-2), 132.5, 130.4 (each C, Ind-C), 129.3, 128.3, 127.5, 127.1, 125.8, 124.4, 123.0 (each CH, Ind-Ar), 122.3 (C, Ind-C), 121.8 (C and CH, Ind-C and C-3), 121.5 (CH, Ind-Ar), 113.3, 113.2, 110.8, 110.2 (each CH, Ind-Cp), 89.9, 89.5 (each C, Ind-C), 67.9 (CH$_2$, C-1), ~24 (CH$_2$, C-4), -2.4, -4.1 (each CH$_3$, Si(CH$_3$)$_2$ ppm, ipso- and p-B(C$_6$F$_5$)$_3$ not detected. ^{19}F NMR (toluene-d_8: C$_6$D$_5$Br = 1:1, 564.3 MHz, 253 K): $\delta = -161.2$ (m, $^3J_{FF} = 21$ Hz, 6F, m-F), -143.0 (t, $^3J_{FF} = 20.5$ Hz, 3F, p-F), -129.4 (d, $^3J_{FF} = 20.5$ Hz, 6F, o-F) ppm. IR (KBr): $\tilde{\nu} = 2964$, 1643, 1514, 1457, 1387, 1263, 1153, 1146, 979, 933, 828, 816, 680 cm^{-1}. Anal. Calcd for C$_{42}$H$_{24}$BF$_{15}$SiZr·C$_6$D$_6$ (1027.9): C, 56.09; H, 3.53. Found: C, 55.20; H, 3.15. X-ray crystal structure analysis of **7**: formula C$_{42}$H$_{24}$-BF$_{15}$SiZr·C$_7$H$_8$, $M = 1035.87$, $0.30 \times 0.25 \times 0.20$ mm, $a = 12.864(1)$ Å, $b = 21.072(3)$ Å, $c = 16.607(2)$ Å, $\beta = 110.34(1)°$, $V = 4221.0(9)$ Å^3, $\rho_{calc} = 1.630$ g cm^{-3}, $\mu = 3.93$ cm^{-1}, empirical absorption correction via φ scan data ($0.895 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 8887 reflections collected ($\pm h$, $+k$, $-l$), $[(\sin \theta)/\lambda] = 0.62$ Å^{-1}, 8583 independent and 4258 observed reflections $[I \geq 2\ \sigma(I)]$, 557 refined parameters, $R = 0.059$, $R_w^2 = 0.134$, max residual electron density 1.02 (-0.85) e Å^{-3}, hydrogens calculated and refined as riding atoms. The data set was collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics DIAMOND and SCHAKAL-92.

Polymerization Reactions. An 1 L glass autoclave was charged with toluene (300 mL) and triisobutylaluminum (0.5 mL). The mixture was stirred (800 rpm), thermostated at 40 °C, and saturated with the gaseous monomer. The polymerization reaction was started by the injection of a toluene solution of betaine complex **7**, generated in situ as described above from 15 mg (34.7 μmol) of **6** in 4 mL of toluene and 22 mg (42.9 μmol) of tris(pentafluorophenyl)borane in 3 mL of toluene. After a given time the reaction was stopped by the addition of methanol (15 mL) acidified with HCl (aq, 2 N, 15 mL). The polymer was precipitated by further addition of aqueous HCl (6 N, 100 mL), collected by filtration, washed with 6 N HCl (50 mL), water (200 mL), and acetone (30 mL), and dried in vacuo to constant weight. Melting points were determined by differential scanning calorimetry using a heating rate of 10 °C/min. The results of the second scan after complete melting and cooling of the samples are reported. ^{13}C NMR spectra of the polypropylene samples were recorded on a Bruker AC 200 P spectrometer (^{13}C: 50.3 MHz) with proton decoupling at 350 K in a solvent mixture of 1,2,4-trichlorobenzene and C$_6$D$_6$ (5:1). Ethene polymerization: reaction time 5 min; p(ethene) = 2 bar; yield 13.39 g; activity 2313 kg PE·mol [Zr]$^{-1}$·h^{-1}·bar^{-1}; melting point 134 °C. Propene polymerizations: reaction time 45 min; p(propene) = 2 bar: yield 63.6 g; activity 1221 kg PP·mol [Zr]$^{-1}$·h^{-1}·bar^{-1}; melting point 132 °C, [mmmm] = 77.5%, [mmmr] = 9.9%, [mmrr] = 8.6%, [mrrm] = 4.0%; p(propene) = 1 bar: yield 29.7 g; activity 1138 kg PP·mol [Zr]$^{-1}$·h^{-1}·bar^{-1}; melting point 132 °C; [mmmm] = 81.2%, [mmmr] = 8.1%, [mmrr] = 7.3%, [mrrm] = 3.4%; p(propene) = 0.5 bar: yield 10.8 g; activity 830 kg PP·mol [Zr]$^{-1}$·h^{-1}·bar^{-1}; melting point 141 °C; [mmmm] = 90.9%, [mmmr] = 4.1%, [mmrr] = 3.6%, [mrrm] = 1.4%. An independent propene polymerization control experiment was carried out using the rac-[Me$_2$Si(1-indenyl)$_2$]ZrCl$_2$/MAO catalyst system according to the procedure described above by replacing the triisobutylaluminum with 20 mL of a 10 weight percent MAO solution in toluene. The reaction was started by injection of a solution of the dichlorozirconium complex (9 mg, 20.1 μmol) in toluene (10 mL): Al/Zr = 1720;

reaction temperature 40 °C; reaction time 45 min; p(propene) = 2 bar; yield 201.8 g; activity 6706 kg PP·mol [Zr]$^{-1}$·h^{-1}·bar^{-1}; melting point 116 °C; [mmmm] = 68.5%, [mmmr] = 14.6%, [mmrr] = 11.7%, [mrrm] = 5.3%.

Stoichiometric Alkene Insertions. General Procedure. An NMR tube filled with a solution of the betaine complex **7** in toluene-d_8, prepared in situ as described above, was placed in a Schlenk flask and cooled to -20 °C. While keeping the NMR tube under an argon atmosphere, 3 mL of the gaseous α-olefin was bubbled through the solution by a capillary. The tube was then sealed, taken out of the Schlenk flask, and kept at -15 °C for 15 h before the NMR spectra were recorded.

Insertion of Ethene into Me$_2$SiInd$_2$Zr(μ-C$_4$H$_6$)B(C$_6$F$_5$)$_3$ (7). Formation of 8. ^{1}H NMR (toluene-d_8, 599.9 MHz, 253 K): $\delta = 7.26$, 7.11, 6.93 (each m, 1H, Ind-Ar), 6.82, 6.73 (each ddd, $^3J = 8.5$, 7.6 Hz, $^4J = 0.9$ Hz, 1H, Ind-Ar), 6.58 (ddd, $^3J = 8.5$, 7.0 Hz, $^4J = 0.9$ Hz, 1H, Ind-Ar), 6.48 (dd, $^3J = 8.8$ Hz, $^4J = 0.9$ Hz, 1H, Ind-Ar), 6.45 (dd, $^3J = 8.5$ Hz, $^4J = 0.9$ Hz, 1H, Ind-Ar), 5.96, 5.91 (each d, $^3J = 3.3$ Hz, 1H, Ind-Cp), 5.87 (m, 1H, 5-H), 5.80 (d, $^3J = 3.3$ Hz, 1H, Ind-Cp), 5.41 (ddd, $^3J = 15.6$, 11.0, 4.3 Hz, 1H, 4-H), 4.66 (d, $^3J = 3.3$ Hz, 1H, Ind-Cp), 1.55 (m, 2H, 2-H and 2-H′), 1.40 (d, $^3J = 11.0$ Hz, 1H, 3-H), 1.15 (broad, 1H, 6-H), 0.82 (m, 1H, 3-H′), 0.39, 0.02 (each s, 3H, Si(CH$_3$)$_2$), -1.01 (broad d, $^2J = 13.3$ Hz, 1H, 1-H), -1.79 (broad, 1H, 6-H′), -1.99 (m, 1H, 1-H′) ppm. ^{13}C NMR (toluene-d_8, 150.8 MHz, 253 K): $\delta = 148.2$ (d, $^1J_{CF} = 250$ Hz, $o-$B(C$_6$F$_5$)$_3$), 141.9 (CH, C-4), 137.3 (d, $^1J_{CF} = 250$ Hz, $m-$B(C$_6$F$_5$)$_3$), 134.2 (CH, C-5), 127.7, 127.6, 127.5, 126.7, 126.5, 126.0, 124.5, 123.1 (each CH, Ind-Ar−CH), 120.5, 113.1, 112.3, 108.6 (each CH, Ind-Cp-CH), 67.8 (CH$_2$, C-1), 38.1 (CH$_2$, C-2), 35.0 (CH$_2$, C-3), ~14 (CH$_2$, C-6), -1.7, -4.1 (each CH$_3$, Si(CH$_3$)$_2$) ppm, ipso and $p-$B(C$_6$F$_5$)$_3$ not detected, quaternary C not assigned.

Insertion of Propene into Me$_2$SiInd$_2$Zr(μ-C$_4$H$_6$)B(C$_6$F$_5$)$_3$ (7). Formation of 9A and 9B. The formation of two diastereomers in a ratio of **A:B** = 60:40 can be observed. Only the signals of the alkyl chain C1−C7 are assigned. ^{1}H NMR (toluene-d_8, 599.9 MHz, 253 K): $\delta = 6.09$ (m, 1H, 5-H, **B**), 5.78 (m, 1H, 5-H, **A**), 5.31 (m, 1H, 4-H, **A**), 4.89 (m, 1H, 4-H, **B**), 1.85 (m, 1H, 2-H, **A**), 1.74 (m, 1H, 1-H, **B**), 1.62 (m, 1H, 3-H, **B**), 1.40 (m, 1H, 3-H, **A**), 1.10 (broad s, 1H, 6-H, **A**), 0.90 (m, 1H, 6-H, **B**), 0.80 (m, 2H, 2-H and 3-H′, **B**), 0.52 (m, 1H, 3-H′, **A**), 0.40 (m, 6H, 7-H, **A** and 7-H, **B**), -1.13 (d, $^2J = 12.5$ Hz, 1H, 1-H, **A**), -1.84 (broad s, 1H, 6-H′, **A**), -2.08 (dd, $^2J = 12.5$ Hz, $^3J = 12.5$ Hz, 1H, 1-H′, **A**), -3.47 (broad d, $^2J = 12.1$ Hz, 1H, 6-H′, **B**), -3.95 (d, $^2J = 12.4$ Hz, 1H, 1-H′, **B**) ppm. ^{13}C NMR (toluene-d_8, 150.8 MHz, 253 K): $\delta = 138.9$ (CH, C-4, **A**), 133.9 (CH, C-5, **A**), 133.4 (CH, C-5, **B**), 77.0 (CH$_2$, C-1, **A**), 67.0 (CH$_2$, C-1, **B**), 49.1 (CH, C-2, **B**), 44.8 (CH, C-2, **A**), 42.5 (CH$_2$, C-3, **A**), 36.3 (CH$_2$, C-3, **B**), 27.5 (CH$_3$, C-7, **B**), 27.1 (CH$_3$, C-7, **A**), ~14 (CH$_2$, C-6, **A** and **B**) ppm, C-4 (**B**) not detected. **10A/10B**: ^{1}H NMR (toluene-d_8/THF-$d_8 \approx$ 10:1, 599.9 MHz, 253 K): $\delta = 4.61$ (m, 1H, 5-H, **B**), 4.41 (m, 1H, 5-H, **A**), 3.53 (m, 1H, 4-H, **B**), 3.11 (m, 1H, 4-H, **A**), 2.60 (m, 1H, 2-H, **A**), 2.28 (m, 1H, 3-H, **A**), 2.07 (m, 1H, 3-H, **B**), 1.66 (broad, 1H, 6-H, **B**), 1.44 (m, 1H, 3-H′, **B**), 1.41 (broad, 1H, 6-H, **A**), 1.09 (m, 1H, 2-H, **B**), 0.95 (m, 3H, 7-H, **A**), 0.94 (m, 1H, 3-H′, **A**), 0.84 (m, 3H, 7-H, **B**), 0.81 (m, 1H, 1-H, **B**), -0.15 (d, $^2J = 12.3$ Hz, 1H, 1-H, **A**), -2.63 (broad d, $^2J = 13.4$ Hz, 1H, 6-H′, **A**), -2.79 (d, $^2J = 11.0$ Hz, 1H, 1-H′, **B**), -3.04 (broad, 1H, 6-H′, **B**), -3.35 (dd, $^2J = 12.3$ Hz, $^3J = 12.3$ Hz, 1H, 1-H′, **A**) ppm. ^{13}C NMR (toluene-d_8: THF-$d_8 \approx$ 10:1, 150.8 MHz, 253 K): $\delta = 120.3$ (CH, C-4, **B**), 119.8 (CH, C-5, **A**), 118.8 (CH, C-4, **A**), 117.7 (CH, C-5, **B**), 58.2 (CH, C-2, **A**), 58.0 (CH, C-2, **B**), 54.3 (CH$_2$, C-1, **A**), 52.3 (CH$_2$, C-6, **B**), 49.1 (CH$_2$, C-6, **A**), 44.9 (CH$_2$, C-1, **B**), 43.2 (CH$_2$, C-3, **A**), 37.2 (CH$_2$, C-3, **B**), 28.8 (CH$_3$, C-7, **B**), 28.5 (CH$_3$, C-7, **A**) ppm (all ^{13}C NMR chemical shifts of **10A/10B** are from the GHSQC experiment).

(1,3-Pentadiene)zirconocene (15). To a mixture of zirconocene dichloride (1.00 g, 3.33 mmol) and lithium sand (67 mg, 10.0 mmol, activated with 2% of sodium) was added ether (50 mL) and pentadiene (0.33 mL, 3.33 mmol, mixture of cis and trans form) at -78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 5 h. The dark suspension was filtered, and the filtrate was evaporated to dryness. The crude reaction product was extracted with pentane (30 mL), and the pentane extract was concen-

trated in vacuo to a volume of 10 mL. The orange (pentadiene)-zirconocene complex **15** was precipitated at −20 °C, collected by filtration, washed with a minimal amount of cold pentane, and dried in vacuo. Yield: 309 mg, (32%); mp 117 °C; 1:1 mixture of s-cis- (**A**) and s-trans-**15** (**B**). ^{1}H NMR (C$_6$D$_6$, 599.9 MHz, 298 K): δ = 5.38, 4.92, 4.86, 4.85 (each s, 5H, cyclopentadienyl H, **A** and **B**), 4.61 (m, 1H, 2-H, **A**), 4.56 (m, 1H, 3-H, **B**), 3.44 (m, 4-H, **A**), 3.13 (dd, ^2J = 4.0 Hz, ^3J = 7.1 Hz, 1H, 4-H, **B**), 2.94 (dd, 2× ^3J = 15.3 Hz, 1H, 2-H, **B**), 2.58 (dddd, ^3J = 16.4, 15.3, 6.1, 1.1 Hz, 1H, 3-H, **B**), 2.05 (d, ^3J = 5.8 Hz, 3H, CH$_3$, **A**), 2.03 (d, ^3J = 6.1 Hz, 3H, CH$_3$, **B**), 1.75 (ddq, ^3J = 15.3 Hz, ^3J = 6.1 Hz, ^4J = 1.1 Hz, 1H, 1-H, **B**), 1.12 (ddd, ^2J = 4.0 Hz, ^3J = 16.4 Hz, ^4J = 1.1 Hz, 1H, 4-H′, **B**), −0.45 (m, 1H, 1-H, **A**), −0.79 (m, 1H, 4-H′, **A**) ppm; ^{13}C NMR (C$_6$D$_6$, 150.8 MHz, 298 K) δ = 116.5 (CH, C-2, **A**), 108.5 (CH, C-3, **A**), 103.6 (CH, cyclopentadienyl C, **A** or **B**), 100.4 (CH, C-2, **B**), 100.1, 99.6, 99.1 (each CH, cyclopentadienyl C, **A** and **B**), 86.7 (CH, C-3, **B**), 76.2 (CH, C-1, **B**), 65.0 (CH, C-1, **A**), 57.4 (CH$_2$, C-4, **B**), 49.9 (CH$_2$, C-4, **A**), 21.4, 21.2 (each CH$_3$, CH$_3$, **A** and **B**) ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2923, 2845, 1439, 1262, 1120, 1096, 1014, 960, 796, 733, 670 cm^{-1}. Anal. Calcd for C$_{15}$H$_{18}$Zr (289.5): C, 62.23; H, 6.27. Found: C, 61.10; H, 5.89.

Generation of Cp$_2$Zr(μ-CH$_3$C$_4$H$_5$)B(C$_6$F$_5$)$_3$ (16). The betaine complex **16** was generated in situ by the addition of a solution of (pentadiene)zirconocene (**15**) (7 mg, 24.2 μmol) in 2 mL of toluene-d_8 to a solution of tris(pentafluorophenyl)borane (12 mg, 24.2 μmol) in 1 mL of toluene-d_8: ^{1}H NMR (toluene-d_8, 599.9 MHz, 298 K) δ = 5.53 (dd, 2× ^3J = 14.6 Hz, 1H, 2-H), 5.26, 5.20 (each s, 5H, cyclopentadienyl-H), 4.39 (m, 1H, 3-H), 2.43 (m, 1H, 1-H), 2.20, 1.54 (each broad d, ^2J = 17.5 Hz, 1H, 4-H, 4-H′), 0.94 (d, ^3J = 6.0 Hz, 3H, CH$_3$) ppm; ^{13}C NMR (toluene-d_8, 150.8 MHz, 298 K) δ = 149.3 (d, $^1J_{CF}$ = 242 Hz, o-B(C$_6$F$_5$)$_3$), 137.8 (d, $^1J_{CF}$ = 249 Hz, p-B(C$_6$F$_5$)$_3$), 137.2 (d, $^1J_{CF}$ = 249 Hz, m-B(C$_6$F$_5$)$_3$), 139.4 (CH, C-2), 111.41, 111.39 (each CH, cyclopentadienyl-C), 105.2 (CH, C-3), 71.1 (CH, C-1), ~26 (CH$_2$, C-4), 19.1 (CH$_3$, CH$_3$) ppm, ipso-B(C$_6$F$_5$)$_3$ not detected.

Propene Insertion into Cp$_2$Zr(μ-CH$_3$C$_4$H$_5$)B(C$_6$F$_5$)$_3$ (16). Formation of 18. An NMR tube filled with a solution of the betaine complex **16** in toluene-d_8, prepared in situ as described above, was placed in a Schlenk flask and cooled to −20 °C. While keeping the NMR tube under an argon atmosphere, 3 mL of the gaseous α olefin was bubbled through the solution by a capillary. The tube was then sealed, taken out of the Schlenk flask, and kept at −15 °C for 15 h before the NMR spectra were measured. ^{1}H NMR (toluene-d_8, 599.9 MHz, 253 K): δ = 5.67 (m, 1H, 5-H), 5.31, 5.08 (each s, 5H, cyclopentadienyl-H), 5.02 (dd, ^3J = 16.1 Hz, ^3J = 10.0 Hz, 1H, 4-H), 1.21 (m, 1H, 2-H), 1.15 (broad, 1H, 6-H), 0.95 (dd, ^2J = 12.8 Hz, ^3J = 12.8 Hz, 1H, 1-H), 0.54 (d, ^3J = 6.3 Hz, 3H, 7-H), 0.39 (m, 1H, 3-H), 0.37 (broad s, 3H, 8-H), −0.48 (broad d, ^2J = 7.9 Hz, 1H, 6-H′), −0.64 (dd, ^2J = 12.8 Hz, ^3J = 1.9 Hz, 1H, 1-H′) ppm. ^{13}C NMR (toluene-d_8, 150.8 MHz, 253 K): δ = 148.3 (d, $^1J_{CF}$ = 250 Hz, o-B(C$_6$F$_5$)$_3$), 143.6 (CH, C-4), 139.2 (d, $^1J_{CF}$ = 250 Hz, p-B(C$_6$F$_5$)$_3$), 137.3 (d, $^1J_{CF}$ = 250 Hz, m-B(C$_6$F$_5$)$_3$), 122.8 (CH, C-5), 111.3, 109.9 (each CH, cyclopentadienyl C), 56.5 (CH$_2$, C-1), 53.6 (CH, C-2), 46.7 (CH, C-3), 25.6 (CH$_3$, C-7), 16.8 (CH$_3$, C-8) ppm, C-6 and ipso-B(C$_6$F$_5$)$_3$ not detected. 1D-ROESY (toluene-d_8, 599.9 MHz, 253 K): irradiation at δ = 1.21 (2-H) ppm NOE enhancement at δ = 5.02 (4-H), 0.54 (7-H), 0.37 (8-H), −0.64 (1-H′) ppm; irradiation at δ = 5.02 (4-H) ppm NOE enhancement at δ = 5.67 (5-H), 5.31, 5.08 (each cyclopentadienyl H), 1.21 (2-H), 0.37 (8-H), −0.48 (6-H′); irradiation at δ = 0.95 (1-H) ppm NOE enhancement at δ = 5.67 (5-H), 5.31 (cyclopentadienyl-H), 0.54 (7-H), 0.39 (3-H), −0.64 (1-H′) ppm. Selective proton decoupling at δ = 0.54 (7-H) ppm leads to a broad pseudo triplet at δ = 1.21 (2-H) ppm with 2× ^{3}J ≈ 10 Hz.

Supporting Information Available: Details of the X-ray crystal structure analysis of complexes **7** and additional spectroscopic information for the metallocene−borate betaines and their alkene insertion products. This material is available free of charge via the Internet at http://pubs.acs.org.

JA983595V