

## (Butadiene)metallocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Pathway to Catalyst Systems for Stereoselective Methyl Methacrylate Polymerization: Evidence for an Anion Dependent Metallocene Catalyzed Polymerization Process

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**Abstract:** The *ansa*-zirconocene dichlorides [Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)(3-R-C<sub>5</sub>H<sub>3</sub>)]ZrCl<sub>2</sub> **7a–e** (R = H, CH<sub>3</sub>, cyclohexyl, –CHMe<sub>2</sub>, –CMe<sub>3</sub>) were reacted with butadiene–magnesium to yield the respective ( $\eta^4$ -butadiene)-metallocenes **17a–e**. The chiral examples give a mixture of two *s*-cis and two *s*-trans diastereomers. The strong Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adds selectively to a terminal butadiene carbon atom to yield the (butadiene)-metallocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> betaine complexes **18a–e**. Initially, the formation of the *Z*-**18** isomers is preferred. These consecutively rearrange to the thermodynamically favored isomers *E*-**18**. The dipolar systems **18** are active single component metallocene catalysts for the stereospecific polymerization of methyl methacrylate. With increasing steric bulk of the attached single alkyl substituent an increasingly isotactic poly(methyl methacrylate) is obtained. A similar trend is observed in the methyl methacrylate polymerization at the [Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)(3-R-C<sub>5</sub>H<sub>3</sub>)]ZrCH<sub>3</sub><sup>+</sup> catalysts (**9a–e**) that were conventionally prepared by methyl abstraction from the corresponding *ansa*-zirconocene dimethyl complexes by treatment with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. A comparison of the poly(methyl methacrylates) obtained at these two series of catalysts has revealed substantial differences in stereoselectivity that probably originate from an influence of the respective counteranions. An initial reactive intermediate of methyl methacrylate addition to the dipolar single component metallocene catalyst *E*-**18a** was experimentally observed and characterized by NMR spectroscopy at 253 K. The subsequently formed series of [PMMA–C<sub>4</sub>H<sub>6</sub>–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> anion oligomers (at the catalyst **18c**) was monitored (after quenching) and characterized by electrospray mass spectrometry.

### Introduction

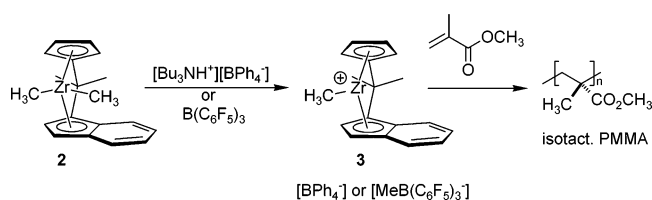
The advent of the group 4 metallocene catalysts has marked the beginning of a remarkable advancement in ethylene and  $\alpha$ -olefin polymerization.<sup>1</sup> Gaining detailed insight into their functioning and the specific mechanistic features that govern the remarkable reactivity/selectivity patterns of this and related classes of catalysts has greatly contributed to the ongoing development of the field.<sup>2–4</sup> In view of the rapid progress that can be followed in metal-catalyzed olefin polymerization and

related catalytic carbon–carbon coupling processes, it seems likely that some of the more resistant problems will see interesting solutions appear in due time. One such area is the involvement of functionalized alkenes in the polymerization process.<sup>5</sup> Yasuda et al.<sup>6,7</sup> showed that metallocenes can play an important role in the rapid and selective carbon–carbon coupling of olefins bearing electron-withdrawing substituents. They demonstrated that (Cp\*<sub>2</sub>SmH)<sub>2</sub> catalyzes the isospecific polymerization of methyl methacrylate. A reaction mechanism was proposed that involved hydride addition to the  $\beta$ -position of

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Scheme 1



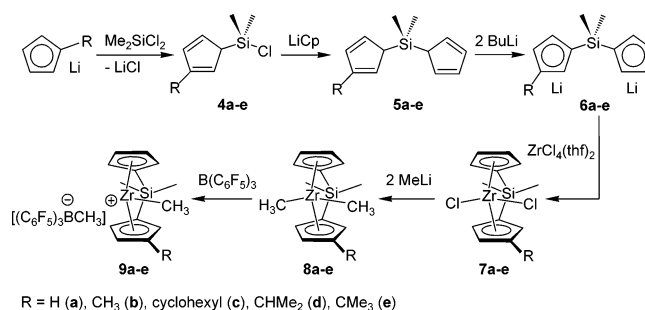
the  $\alpha,\beta$ -unsaturated carbonyl compound followed by enolate addition to the coordinated monomer. The chain growth would then take place by a series of repetitive enolate Michael additions via an eight-membered transition state<sup>8</sup> at the samarium center.

Collins et al. showed that methyl methacrylate (MMA) is polymerized using alkylmetallocene cation Ziegler–Natta type catalysts.<sup>9</sup> In a series of papers they convincingly showed that this polymerization reaction is taking place by a group transfer type process that involves the active participation of a pair of metallocene moieties.<sup>10</sup> Isotactic poly(methyl methacrylate) (PMMA) is formed at Brintzinger's *ansa*-zirconocene [(ethylene)bis-indenyl]ZrCH<sub>3</sub><sup>+</sup>, but the catalytic procedure developed by Soga et al.<sup>11</sup> requires the use of a large excess of a dialkylzinc (ca. 1000 equiv was used).

Recently, independent studies by Höcker et al.<sup>12–14</sup> and Gibson et al.<sup>15</sup> have shown that chiral catalysts derived from Green's *ansa*-metallocene (**1**),<sup>16</sup> which exhibit C<sub>1</sub> molecular symmetry, can effectively be used for making isotactic PMMA, provided that a suitable activation procedure was used<sup>17</sup> (see Scheme 1).

A variety of alkyl-substituted dimethylsilanediyl bridged homogeneous *ansa*-metallocene catalysts had previously been used in stereoselective propene polymerization.<sup>18</sup> We have taken up this work and prepared a series of such complexes bearing alkyl groups of increasing steric bulk at one of their *ansa* connected Cp rings and used them for stereoselective MMA polymerization after suitable catalyst activation. A series of catalysts was activated by means of the conventional dimeth-

Scheme 2



ylzirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> route.<sup>17,19</sup> This was complemented by preparing the corresponding butadiene complexes and adding B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to them.<sup>20</sup> This led to active homogeneous single-component catalysts, which produced isotactic PMMA under suitable conditions. However, the obtained PMMA samples from both series of catalysts, using the same backbone variations, exhibited remarkable differences in detail. This may indicate an active involvement of the respective anion in the isospecific PMMA formation at these types of homogeneous metallocene catalyst systems, which shall be discussed on the basis of the experimental evidence presented in this article.

## Results and Discussion

**Preparation of the Catalyst Systems.** The synthesis of the dimethylsilanediyl bridged *ansa*-metallocenes was carried out along the synthetic pathway described in the literature<sup>18,21</sup> for the corresponding dichlorozirconocenes. Dimethyldichlorosilane was treated with one molar equivalent of the respective [(C<sub>5</sub>H<sub>4</sub>R)Li] reagent to yield the silane derivatives **4**. These were isolated and then treated subsequently with 1 equiv of lithium cyclopentadienide to yield **5** (as a mixture of isomers). This order of the nucleophilic substitution reactions prevented the formation of the unsubstituted [C<sub>5</sub>H<sub>4</sub>–SiMe<sub>2</sub>–C<sub>5</sub>H<sub>4</sub>] as a minor side product and resulted in a clean product formation in good yield. Deprotonation of both cyclopentadienyl ring systems in **5** was effected by treatment with *n*-butyllithium in ether at low temperature. The resulting dilithiobis(cyclopentadienide) reagents **6** were isolated in good yield as air- and moisture-sensitive compounds and adequately characterized (for details see the Supporting Information). Transmetalation to zirconium was carried out by treatment of **6** with [ZrCl<sub>4</sub>(thf)<sub>2</sub>] in toluene (–78 °C to room temperature). The *ansa*-zirconocene dichloride complexes **7a–e** (see Scheme 2) were each isolated in ca. 60% yield. They were then each treated with two molar equivalents of methyllithium to yield the corresponding dimethyl *ansa*-zirconocenes **8a–e**.

As expected, the chiral *ansa*-zirconocene dimethyl complex **8e** (R = *tert*-butyl) shows four separate methine <sup>1</sup>H NMR signals (at  $\delta$  6.74, 6.56, 5.58, 5.36; corresponding <sup>13</sup>C NMR signals at  $\delta$  122.2, 119.6, 114.4, 110.4) and three <sup>1</sup>H NMR resonances of the CH groups of the *tert*-butyl substituted Cp ring (at  $\delta$  6.67,

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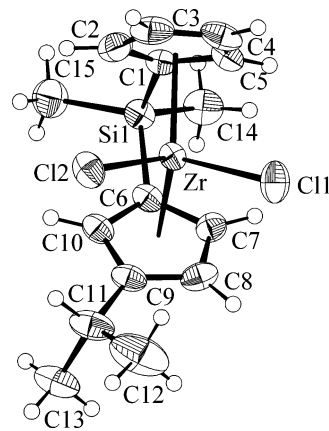
5.62, 5.32;  $^{13}\text{C}$ : 120.1, 111.9, 110.2). Complex **8e** exhibits the NMR signals of a pair of diastereotopic methyl groups at zirconium ( $^1\text{H}$ :  $\delta$  0.01, 0.00;  $^{13}\text{C}$ :  $\delta$  31.6, 28.2) in addition to the *tert*-butyl NMR features [ $^1\text{H}$ :  $\delta$  1.37;  $^{13}\text{C}$ :  $\delta$  33.4 ( $\text{C}(\text{CH}_3)_3$ ), 31.3 ( $\text{CH}_3$ )].

The two *ansa*-zirconocene dichlorides bearing the most bulky substituents, the isopropyl and *tert*-butyl substituted systems **7d** and **7e**, were characterized by X-ray diffraction. Single crystals of **7d** were obtained from toluene. The structure of **7d** shows the typical strained geometry of a silanediyl bridged *ansa*-metallocene. The connection of the Cp rings by the  $\text{SiMe}_2$  group ( $\text{Si}-\text{C}1$  1.870(3) Å,  $\text{Si}-\text{C}6$  1.867(3) Å) results in some characteristic distortions of the complex framework. Consequently, the  $\text{Zr}-\text{C}(\textit{ipso}\text{-Cp})$  bonds are rather short at 2.470(2) Å ( $\text{Zr}-\text{C}6$ ) and 2.484(2) Å ( $\text{Zr}-\text{C}1$ ), whereas the distance between the metal and the Cp carbon that bears the isopropyl substituent is the longest  $\text{Zr}-\text{C}(\text{Cp})$  bond found at  $d(\text{Zr}-\text{C}9)$ : 2.592(2) Å. The bulky isopropyl group at C9 is effectively shielding the  $\text{Zr}-\text{C}12$  vector (dihedral angle  $\theta$   $\text{C}12-\text{Zr}\cdots\text{C}9-\text{C}11$   $-19.9(2)^\circ$ ). In **7d** the  $\text{Zr}-\text{C}11$  (2.436(1) Å) and  $\text{Zr}-\text{C}12$  (2.433(1) Å) bond lengths are in the typical range (angle  $\text{C}11-\text{Zr}-\text{C}12$   $98.28(3)^\circ$ ).<sup>22</sup> The endocyclic and exocyclic angles at the bridging silicon atom are very different from each other ( $\text{C}1-\text{Si}-\text{C}6$   $94.3(1)^\circ$ ,  $\text{C}14-\text{Si}-\text{C}15$   $114.8(1)^\circ$ ). The Cp-(centroid)- $\text{Zr}$ -Cp(centroid) angle in **7d** amounts to  $126.3^\circ$ .

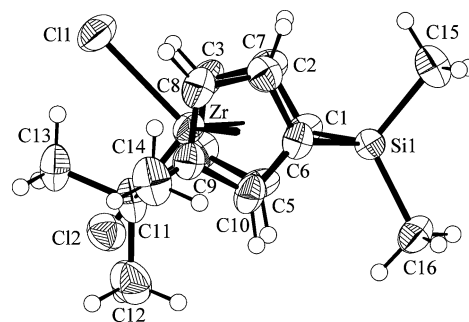
The *tert*-butyl substituted complex **7e** was crystallized from pentane. In the crystal we find a 72:28 mixture of the two enantiomers. The Cp(centroid)- $\text{Zr}$ -Cp(centroid) angles are similar for both the major isomer ( $126.2^\circ$ ) and the minor isomer ( $125.1^\circ$ ). The representative data of the major enantiomer will be discussed. The overall structure is similar to that of **7d** (see above); however, the more bulky *tert*-butyl group seems to further distort the *ansa*-metallocene framework. This is most apparent for the  $\text{Zr}-\text{C}(\text{Cp})$  distances. Again, the range of observed  $\text{Zr}-\text{C}(\text{Cp})$  bond lengths is rather large with  $\text{Zr}-\text{C}1$  being the shortest at 2.449(19) Å. The longest  $\text{Zr}-\text{C}(\text{Cp})$  bond is between the metal center and carbon atom C9 (2.633(10) Å), which bears the bulky *tert*-butyl group. It is ca. 0.04 Å longer than the respective bond in **7d**. The remaining structural features of **7e** are similar to those of **7d** (see Figure 2). The *tert*-butyl group in **7e** is oriented such that it very effectively shields the  $\text{Zr}-\text{C}12$  vector from the outside ( $\theta$   $\text{C}12-\text{Zr}\cdots\text{C}9-\text{C}11$   $-25.5(15)^\circ$ ).

The structure of the isopropylidene bridged (Cp/indenyl)-zirconium dimethyl complex **2** was characterized by X-ray diffraction for comparison. Despite the presence of shorter bridging bonds, some essential structural features of **2** closely resemble those of **7e**. Again the  $\text{Zr}-\text{C}(\textit{ipso}\text{-Cp})$  bonds at the bridge are short ( $\text{Zr}-\text{C}19$  2.456(2) Å,  $\text{Zr}-\text{C}23$  2.463(3) Å). The  $\text{Zr}-\text{C}13$  bond length (2.642(2) Å) marks the top end of the  $\text{Zr}-\text{C}(\text{Cp})$  range in **2**. Its position is equivalent to that of the substituent-bearing C(Cp) atom in **7e**, and these specific  $\text{Zr}-\text{C}(\text{Cp})$  bond lengths of the molecules **2** and **7e** are almost identical. The remaining structural features of complex **2** are as expected (see Figure 3).

We next activated the complexes **8a-e** by removing one methyl anion equivalent from zirconium by treatment with a stoichiometric amount of the strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>17a,19</sup> For this study we did not actually isolate the corresponding



**Figure 1.** Molecular geometry of complex **7d**. Selected bond lengths (angstroms) and angles (deg):  $\text{Zr}-\text{C}11$  2.436(1),  $\text{Zr}-\text{C}12$  2.433(1),  $\text{Zr}-\text{C}1$  2.484(2),  $\text{Zr}-\text{C}2$  2.488(3),  $\text{Zr}-\text{C}3$  2.556(3),  $\text{Zr}-\text{C}4$  2.551(3),  $\text{Zr}-\text{C}5$  2.472(2),  $\text{Zr}-\text{C}6$  2.470(2),  $\text{Zr}-\text{C}7$  2.467(2),  $\text{Zr}-\text{C}8$  2.562(3),  $\text{Zr}-\text{C}9$  2.592(2),  $\text{Zr}-\text{C}10$  2.485(2),  $\text{Si}1-\text{C}1$  1.870(3),  $\text{Si}1-\text{C}6$  1.867(3),  $\text{Si}1-\text{C}14$  1.849(3),  $\text{Si}1-\text{C}15$  1.852(3),  $\text{C}9-\text{C}11$  1.511(3),  $\text{C}11-\text{C}12$  1.520(5),  $\text{C}11-\text{C}13$  1.519(4),  $\text{C}11-\text{Zr}-\text{C}12$   $98.28(3)$ ,  $\text{C}1-\text{Si}1-\text{C}6$   $94.3(1)$ ,  $\text{C}1-\text{Si}1-\text{C}14$   $113.4(1)$ ,  $\text{C}1-\text{Si}1-\text{C}15$   $110.6(1)$ ,  $\text{C}6-\text{Si}1-\text{C}14$   $110.8(1)$ ,  $\text{C}6-\text{Si}1-\text{C}15$   $111.3(1)$ ,  $\text{C}14-\text{Si}1-\text{C}15$   $114.8(1)$ ,  $\text{C}8-\text{C}9-\text{C}10$   $106.9(2)$ ,  $\text{C}8-\text{C}9-\text{C}11$   $127.4(3)$ ,  $\text{C}10-\text{C}9-\text{C}11$   $125.6(2)$ ,  $\text{C}9-\text{C}11-\text{C}12$   $112.1(3)$ ,  $\text{C}9-\text{C}11-\text{C}13$   $109.7(2)$ ,  $\text{C}12-\text{C}11-\text{C}13$   $111.4(3)$ .

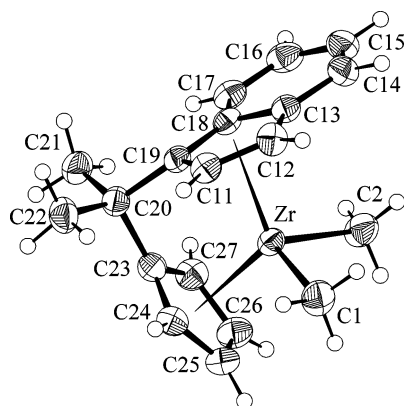


**Figure 2.** Molecular geometry of complex **7e**. Selected bond lengths (angstroms) and angles (deg) (major isomer):  $\text{Zr}-\text{C}11$  2.424(4),  $\text{Zr}-\text{C}12$  2.432(5),  $\text{Zr}-\text{C}1$  2.476(11),  $\text{Zr}-\text{C}2$  2.449(19),  $\text{Zr}-\text{C}3$  2.534(13),  $\text{Zr}-\text{C}4$  2.565(13),  $\text{Zr}-\text{C}5$  2.494(16),  $\text{Zr}-\text{C}6$  2.462(2),  $\text{Zr}-\text{C}7$  2.460(11),  $\text{Zr}-\text{C}8$  2.582(11),  $\text{Zr}-\text{C}9$  2.633(10),  $\text{Zr}-\text{C}10$  2.513(10),  $\text{Si}1-\text{C}1$  1.868(11),  $\text{Si}1-\text{C}6$  1.859(12),  $\text{Si}1-\text{C}15$  1.839(16),  $\text{Si}1-\text{C}16$  1.851(16),  $\text{C}9-\text{C}11$  1.533(16),  $\text{C}11-\text{C}12$  1.51(2),  $\text{C}11-\text{C}13$  1.545(18),  $\text{C}11-\text{C}14$  1.57(2),  $\text{C}11-\text{Zr}-\text{C}12$   $97.5(2)$ ,  $\text{C}1-\text{Si}1-\text{C}6$   $93.8(5)$ ,  $\text{C}1-\text{Si}1-\text{C}15$   $111.7(9)$ ,  $\text{C}1-\text{Si}1-\text{C}16$   $112.7(8)$ ,  $\text{C}6-\text{Si}1-\text{C}15$   $111.0(7)$ ,  $\text{C}6-\text{Si}1-\text{C}16$   $111.8(8)$ ,  $\text{C}15-\text{Si}1-\text{C}16$   $114.2(8)$ ,  $\text{C}8-\text{C}9-\text{C}10$   $106.5(11)$ ,  $\text{C}8-\text{C}9-\text{C}11$   $126.6(13)$ ,  $\text{C}10-\text{C}9-\text{C}11$   $126.2(15)$ ,  $\text{C}9-\text{C}11-\text{C}12$   $114.2(14)$ ,  $\text{C}9-\text{C}11-\text{C}13$   $110.2(13)$ ,  $\text{C}9-\text{C}11-\text{C}14$   $104.7(12)$ ,  $\text{C}12-\text{C}11-\text{C}13$   $111.2(15)$ ,  $\text{C}12-\text{C}11-\text{C}14$   $109.7(13)$ ,  $\text{C}13-\text{C}11-\text{C}14$   $106.5(15)$ .

methyl *ansa*-zirconocene cation products (**9a-e**) but generated them in situ for carrying out the methyl methacrylate polymerization experiments. For their spectroscopic identification we, however, generated them in  $[\text{D}_6]$ benzene. In each case we observed a single set of NMR signals that probably originates from a pair of ion pairs that rapidly equilibrates under the conditions of our measurement.<sup>23</sup> A typical example is the isopropyl substituted product **9d** that exhibits a total of seven Cp-type methine  $^1\text{H}$  NMR resonances [ $\delta$  6.43, 6.30, 5.36, 4.82 ( $\text{C}_5\text{H}_4$ );  $\delta$  6.23, 5.38, 4.78 ( $\text{C}_5\text{H}_3$ )] in addition to the  $^1\text{H}$  NMR

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**Figure 3.** Molecular geometry of complex **2**. Selected bond lengths (angstroms) and angles (deg): Zr–C1 2.263(3), Zr–C2 2.261(3), Zr–C23 2.463(3), Zr–C24 2.474(3), Zr–C25 2.558(3), Zr–C26 2.571(3), Zr–C27 2.494(3), Zr–C19 2.456(2), Zr–C11 2.487(2), Zr–C12 2.583(3), Zr–C13 2.642(2), Zr–C18 2.551(2), C20–C23 1.530(3), C20–C19 1.537(4), C20–C21 1.536(3), C20–C22 1.536(4), C1–Zr–C2 102.8(1), C23–C20–C19 100.8(2), C23–C20–C21 111.6(2), C23–C20–C22 111.3(2), C19–C20–C21 114.0(2), C19–C20–C22 111.5(2), C21–C20–C22 107.7(2).

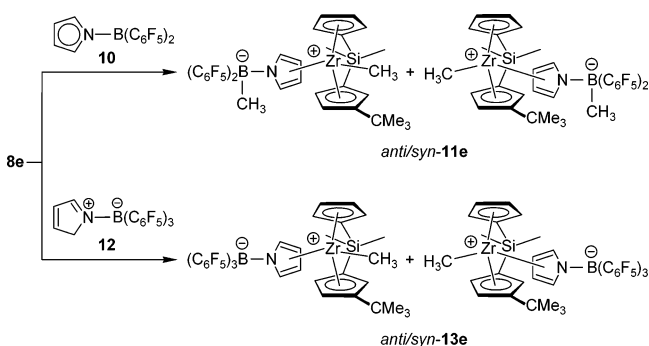
signals of a pair of methyl groups at silicon ( $\delta$  0.02,  $-0.21$ ) and a single Zr–CH<sub>3</sub> signal of 3 H relative intensity at  $\delta$  0.29. The isopropyl methyl groups are diastereotopic (a pair of doublets at  $\delta$  0.90, 0.88). The corresponding [CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> anion shows a broad methyl <sup>1</sup>H NMR resonance at  $\delta$  0.50 (for further details see the Experimental Section).

We had previously shown that *N*-pyrrolyl based borate anions bind slightly stronger to zirconocene cations than the often used [CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> system.<sup>24</sup> We, therefore, treated the *tert*-butyl substituted dimethyl *ansa*-zirconocene complex **8e** with one molar equivalent of the slightly less electron-deficient Lewis acid (*N*-pyrrolyl)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**10**).<sup>24</sup> A methyl anion equivalent was cleanly transferred from zirconium to boron to yield the product **11e**. In this case the ion pair was persistent at room temperature, giving rise to the observation of two isomers (*anti*-**11e**, *syn*-**11e**) by NMR spectroscopy in a ratio of 3:1. The cation moieties of each isomeric ion pair shows the characteristic set of seven Cp methine (CH) <sup>1</sup>H/<sup>13</sup>C NMR signals (for values see the Experimental Section). Due to the chirality of the system and the persistence of the ion pairs, we observed a set of four pyrrolyl CH NMR resonances for each of the isomers [major **11e** isomer:  $\delta$  7.40, 7.32, 5.91, 5.44 (<sup>1</sup>H),  $\delta$  140.3, 136.3, 103.8, 97.5 (<sup>13</sup>C); minor **11e** isomer:  $\delta$  7.48, 7.46, 6.03, 5.92 (<sup>1</sup>H)].

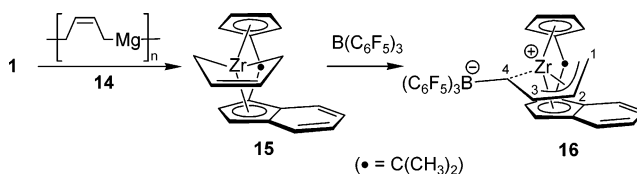
A similar product mixture of the related ion pairs *anti*-**13e** and *syn*-**13e** (4:1) was formed upon treatment of **8e** with the mild neutral Brønsted acid (2*H*-pyrrol)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**12**).<sup>25</sup> In this case, protonation of the [Zr]Me<sub>2</sub> unit occurs to liberate 1 equiv of methane. Again the remaining pyrrolyl moiety at boron coordinated to zirconium was shown to give a persistent pair of stereoisomeric ion pairs. Each of these exhibits the characteristic set of two pairs of diastereotopic pyrrolyl methine groups that are monitored by NMR spectroscopy (see Scheme 3).

We had previously shown that the reference system **1** reacts with the “butadiene–magnesium” reagent (**14**)<sup>26</sup> to yield an (*s*-

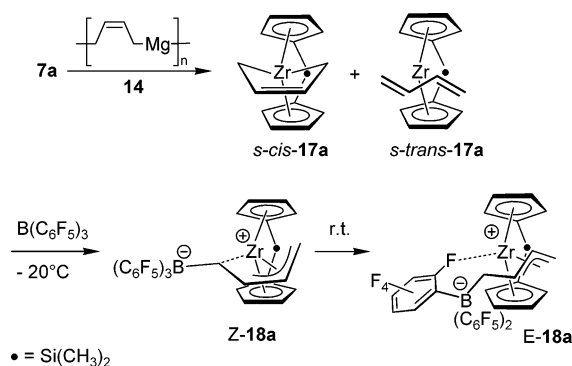
### Scheme 3



### Scheme 4



### Scheme 5



*cis*- $\eta^4$ -butadiene)metallocene complex **15**.<sup>27</sup> To this B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adds selectively to yield a single dipolar betaine complex isomer (**16**) whose specific structure had been revealed by an X-ray crystal structure analysis and confirmed by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy in solution (Scheme 4).<sup>27</sup>

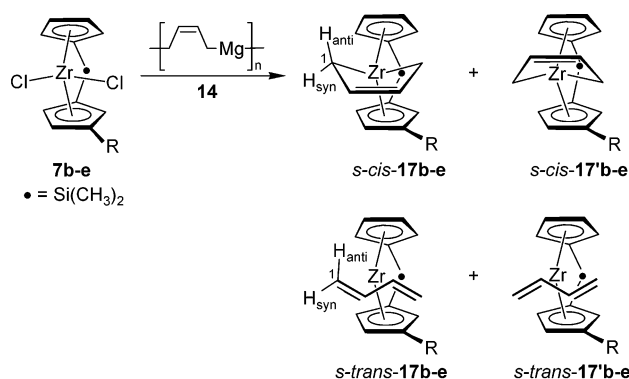
In contrast, the dimethylsilanediyl bridged *ansa*-zirconocenedichloride (**7a**) forms a ca. 1:1 mixture of the (*s*-*cis*- and *s*-*trans*- $\eta^4$ -butadiene)zirconocene (*s*-*cis*-**17a**, *s*-*trans*-**17a**) isomers<sup>28</sup> when treated with “butadiene–magnesium”. These complexes react with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (in a 1:1 stoichiometry) to yield a single *cis*-substituted  $\pi$ -allyl betaine metallocene isomer (**Z-18a**) under kinetic control that subsequently rearranges (at room temperature) to yield the *transoid*  $\pi$ -allyl betaine metallocene isomer (**E-18a**) under equilibrium conditions (see Scheme 5). The complexes **16** and **Z-18** both feature an internal Zr $\cdots$ CH<sub>2</sub>–ion pair interaction, whereas the systems **E-18** are stabilized by an intramolecular Zr $\cdots$ F–C(Ar) coordination.<sup>29</sup>

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Scheme 6



R = CH<sub>3</sub> (b), cyclohexyl (c), CHMe<sub>2</sub> (d), CMe<sub>3</sub> (e)

**Table 1.** Ratios of (*s-cis*- and *s-trans*-Butadiene) *ansa*-Metallocene Isomers **17/17'**<sup>a</sup>

compd	R	<i>s-cis</i> / <i>s-trans</i>	<i>s-cis</i> - <b>17/17'</b>	<i>s-trans</i> - <b>17/17'</b>	T <sup>b</sup> (K)
<b>17b</b>	CH <sub>3</sub>	95:5	4:1	5:1	268
<b>17c</b>	C <sub>6</sub> H <sub>11</sub>	98:2	4:1	c	228
<b>17d</b>	CHMe <sub>2</sub>	97:3	3:1	5:1	248
<b>17e</b>	CMe <sub>3</sub>	99:1	1:1	c	253

<sup>a</sup> Ratios determined by <sup>1</sup>H NMR integration in [D<sub>8</sub>]toluene. <sup>b</sup> Temperature at which the *s-cis*-**17/17'** ratio was determined. <sup>c</sup> Not determined.

The stereochemical situation becomes more complex when a single alkyl substituent is present at the [Cp–SiMe<sub>2</sub>–Cp]-type ligand framework. The reaction of the “butadiene–magnesium” reagent (**14**) with the monoalkyl substituted *ansa*-metallocene dichlorides (**7b–e**) now yields a set of four diastereoisomeric ( $\eta^4$ -butadiene)zirconocene complexes, namely a pair of *s-cis* isomers and a pair of *s-trans* isomers (see Scheme 6). In each case all four complexes are actually found under conditions where the rapid mutual interconversion of the *s-cis* isomers is sufficiently slow to allow for their experimental observation by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy. The attachment of the alkyl substituent at one of the Cp rings has a profound influence on the *s-cis*/*s-trans* isomer equilibrium state.<sup>30</sup> In contrast to the parent system (**7a**) the reaction of **7b–e** with “butadiene–magnesium” gave predominately the (*s-cis*-butadiene)zirconocene products (*s-cis*-**17b–e**, *s-cis*-**17'b–e**) and only small amounts of their respective *s-trans* isomers (*s-trans*-**17b–e**, *s-trans*-**17'b–e**; see Scheme 6 and Table 1). The (*s-cis*-butadiene)zirconocene isomers are rapidly interconverting on the NMR time scale around ambient temperature. For the example of the *tert*-butyl substituted system (*s-cis*-**17e**  $\rightleftharpoons$  *s-cis*-**17'e**), the activation barrier of this “ring-flip” isomerization was determined by dynamic <sup>1</sup>H NMR spectroscopy following the coalescence of their *tert*-butyl resonances (600 MHz, T<sub>coal</sub> = 313 K,  $\Delta G^\ddagger(T_{\text{coal}}) = 14.7 \pm 0.3$  kcal mol<sup>-1</sup>). Most of the isomers

(**17**, **17'**) could be characterized from the respective isomer mixtures by their very characteristic <sup>1</sup>H/<sup>13</sup>C NMR features<sup>30</sup> (see Table 2).

Due to the C<sub>1</sub> chirality of their *ansa*-metallocene backbones, the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> addition to the (butadiene)metallocene systems **17b–e** could in principle give rise to the formation of a total of eight *ansa*-zirconocene(butadiene)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> betaine complex diastereoisomers, namely four inequivalent *Z*-**18b–e** isomers and four inequivalent *E*-**18b–e** isomers. Fortunately, the systems have turned out to show a considerable stereoselectivity. It seems that in each case a single *Z*-**18b–e** isomer is formed which we tentatively assign the structure shown in Scheme 7, in analogy to the reference system **16** (see Scheme 4) that had been characterized by X-ray diffraction.<sup>27</sup> Under the conditions of the preparative B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> addition, the kinetic products *Z*-**18b–e** rapidly rearrange to their favored *E*-**18b–e** isomers,<sup>31</sup> which are the only products that remain after some time. Again, the outcome of the rearrangement is quite stereoselective: in the cases **18c–e** we observe only a single isomer to be formed under thermodynamic control to which we tentatively assign the structures shown in Scheme 7. Only in the case of the methyl substituted system **18b** do we observe a second isomer (*E*-**18'b**) under equilibrium conditions (*E*-**18b**:*E*-**18'b** = 4:1). The transoid *E*-**18** isomers can readily be identified by their typical set of *E*- $\pi$ -allyl <sup>1</sup>H NMR coupling constants (*E*-**18a**: <sup>3</sup>J(1-H<sub>syn</sub>,2-H) = 9.6 Hz, <sup>3</sup>J(1-H<sub>anti</sub>,2-H) = 14.8 Hz, <sup>3</sup>J(2-H;3-H) = 16.2 Hz). The *E*-**18** and *Z*-**18** complex series has easily been distinguished by the characteristically different 4-H/H' <sup>1</sup>H NMR chemical shifts: the *Z*-**18** series has the H<sub>2</sub>C-4 group connected to the early metal center, which gives rise to a large shifting of the 4-H/H' resonances to negative  $\delta$ -values ( $\Delta\delta$  between –3 and –4 ppm relative to the *E*-**18** isomers, see Table 3).

**Methyl Methacrylate Polymerization.** Polymerization experiments were carried out with both series of cations (respectively their ion pairs), namely the methylzirconocene cation series **9a–e** and the (butadiene)zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> series **18a–e**. In addition, we used the previously reported system **3** (see Scheme 1)<sup>12,15</sup> and its (butadiene)metallocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> betaine analogue (**16**)<sup>27</sup> as a reference for comparison.

The MMA polymerization reactions using the **9a–e** catalysts were carried out at 0 °C in dichloromethane solution. The polymerization reactions were allowed to proceed for 1 h and then quenched. The overall catalyst activities were determined by the amount of monomer that had been converted during this period of time. The resulting PMMA was isolated. Its stereochemical composition was determined by <sup>1</sup>H NMR spectroscopy.<sup>32</sup> The proton NMR spectrum shows an AX system at  $\delta$  2.19 and 1.48 (<sup>2</sup>J<sub>HH</sub> = 15 Hz) of the CH<sub>2</sub> group of the m diad of the polymer backbone and a methyl ester resonance at  $\delta$  3.56 (3H). The remaining CH<sub>3</sub> substituent at the quaternary center shows a clean triad splitting under the conditions of this NMR analysis (600 MHz, 298 K, [D]chloroform) and gives rise to separate signals of the mm ( $\delta$  1.17), mr ( $\delta$  0.99), and rr (0.79) triads. The relative intensities of these signals were used to characterize the degree of isotacticity of the samples.

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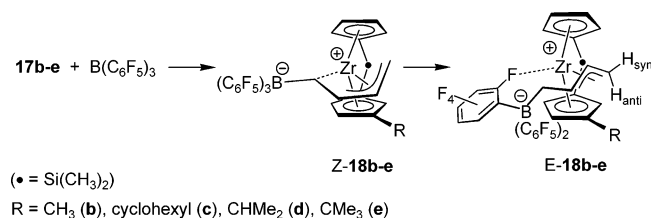
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**Table 2.** NMR Spectroscopic Characterization of (*s-cis*- and *s-trans*-Butadiene) *ansa*-Zirconocene Isomers **17/17'**:  $^1\text{H}/^{13}\text{C}$  NMR Chemical Shifts of  $\eta^4$ -Butadiene Ligand Signals<sup>a</sup>

compd	2-H	3-H	1-H <sub>syn</sub>	4-H <sub>syn</sub>	1-H <sub>anti</sub>	4-H <sub>anti</sub>	C2	C3	C1	C4
<i>s-cis</i> - <b>17b</b>	4.69	4.79	3.36	3.37	-0.76	-1.50	110.1	112.3	49.5	54.1
<i>s-cis</i> - <b>17b'</b>	4.71	4.80	3.43	3.12	-0.83	-0.88	112.0	112.7	50.6	51.9
<i>s-trans</i> - <b>17b</b>	2.89, 2.35 <sup>b</sup>		3.08, 2.61		1.30, 1.23		96.5, 95.0		60.5, 59.8	
<i>s-trans</i> - <b>17b'</b>	2.90, 2.55		3.16, 2.77		1.33, 1.29					
<i>s-cis</i> - <b>17c</b>	4.66	4.76	3.35	3.44	-0.73	-1.45	109.2	112.7	50.1	54.1
<i>s-cis</i> - <b>17c'</b>	4.70	4.83	3.22	3.46	-0.77	-0.88	111.6	112.1	50.7	52.3
<i>s-cis</i> - <b>17d</b>	4.66	4.78	3.36	3.40	-0.78	-1.45	109.8	112.7	50.1	54.0
<i>s-cis</i> - <b>17d'</b>	4.79	4.83	3.41	3.20	-0.79	-0.91	111.2	112.3	50.6	52.5
<i>s-trans</i> - <b>17d</b>	2.88, 2.55		3.16, 2.61		1.38, 1.23		98.1, 97.9		61.2, 60.8	
<i>s-trans</i> - <b>17d'</b>	3.30, 2.68		3.24, 2.97		1.43, 1.32					
<i>s-cis</i> - <b>17e</b>	4.62	4.73	3.42	3.27	-0.72	-0.86	110.1	112.1	51.4	51.6
<i>s-cis</i> - <b>17e'</b>	4.67	5.14	3.25	3.47	-0.70	-0.96	109.1	113.4	50.3	52.1

<sup>a</sup> In [D<sub>8</sub>]toluene at the temperature given in Table 1, at 600 MHz ( $^1\text{H}$ ), 150.8 MHz ( $^{13}\text{C}$ ). <sup>b</sup> Relative assignment.

**Scheme 7**

The complexes **9** are all rather active methyl methacrylate polymerization catalysts, as can be seen from the data compiled in Table 4. However, under the applied conditions they seem to be slightly less active as compared to the “Gibson/Höcker” system (**3**).<sup>12,15</sup> Ion pairing<sup>23,33</sup> can have a strong adverse effect: the strongly ion paired<sup>24,25</sup> systems **11e** and **13e** (see Scheme 3) are inactive under the analogous reaction conditions. The bulk of the substituent attached at one of the Cp rings of the systems **9** has a very profound influence on the features of the polymerization reaction. Most profound (and expected) is its control over the stereochemistry of the MMA polymerization process. Polymerization of methyl methacrylate with the unsubstituted catalyst system **9a** (R = H) proceeds to yield a markedly syndiotactic poly(methyl methacrylate) product, with the stereochemical outcome probably being dominated by chain end control.<sup>9,11,34</sup> This is already turned over to the isotactic regime upon attachment of the relatively small CH<sub>3</sub> group to a Cp ring at the catalyst backbone (**9b**, see Table 4).<sup>35</sup> Consequently, the isotacticity of the resulting PMMA is markedly increased with increasing steric bulk of that single alkyl substituent at the ligand backbone on going from cyclohexyl

(**9c**) to the isopropyl (**9d**) and *tert*-butyl substituted system (**9d**). Although the latter are slightly less active than the system **3**, used as a reference, they seem to slightly exceed it with regard to isotactic stereocontrol under the polymerization reaction conditions that we have here applied. Figure 4 visualizes the pronounced substituent effect of the catalysts **9** on the resulting isotactic poly(methyl methacrylates) showing the change in relative intensities of the  $^1\text{H}$  NMR triad signals of the angular methyl substituent at the polymer chain.

The (butadiene)zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> betaine systems<sup>36</sup> are also active catalysts for methyl methacrylate polymerization. Overall, the (butadiene)zirconocene derived catalysts seem to be less active. This is hardly noticed with the generally very active [(isopropylidene)Cp(indenyl)]Zr system, but becomes very noteworthy with the less active series of the [(dimethylsilyl)diyl](Cp)(CpR)]Zr systems. The catalysts **18** exhibit only about half the activities as the more conventional catalyst systems **9** (see Tables 4 and 5).<sup>35</sup> There is a very pronounced dependence of the stereochemistry of PMMA formation on the method of catalyst formation. As expected, the unsubstituted parent (butadiene)-*ansa*-zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst (**18a**) shows no enantiomorphic site control on PMMA formation. A partially syndiotactic PMMA has been obtained, which is typical for this situation. The gradual turnover to isotactic poly(methyl methacrylate) formation with increasing steric bulk of the alkyl substituent at the *ansa*-metallocene backbone is also observed for the systems **18b–e**, but it is much less pronounced than with their **9b–e** analogues (see Tables 4 and 5). In each of the respective catalyst pairs **18/9** the poly(methyl methacrylates) derived from the (butadiene)metallocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> betaine catalyst systems show markedly lower isotacticities than those obtained from the [(methyl)metallocene]<sup>+</sup>[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> catalysts. The  $^1\text{H}$  NMR methyl triad signal sections of the respective polymers shown in Figure 5 visualize this effect. However, the (butadiene)metallocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> method does not necessarily lead to lower stereocontrol in general: the **16** derived PMMA has turned out to be even slightly more isotactic than the PMMA obtained at the conventional catalyst system **3** (see Figure 5, Tables 4 and 5).

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**Table 3.** Comparison of  $^1\text{H}/^{13}\text{C}$  NMR Features of the  $[\text{B}]-\text{CH}_2-\text{C}_6\text{H}_4$  Moiety of Complexes **Z-18(b-e)** and **E-18(b-e)**<sup>a</sup>

compd/R	1-H <sub>syn</sub>	1-H <sub>anti</sub>	2-H	3-H	4-H	4-H'	C1	C2	C3	C4 <sup>b</sup>
<b>Z-18b</b> /CH <sub>3</sub>	2.62	0.27	5.16	4.49	-0.43	-1.83	55.0	131.4	117.9	25
<b>E-18b</b> /CH <sub>3</sub>	1.61	1.33	5.91	4.69	2.50	2.21	53.5	132.5	120.5	27
<b>E-18b'</b> /CH <sub>3</sub>	1.48	1.67	5.70	5.38	2.51	2.18	51.4	129.1	114.4	27
<b>Z-18c</b> /C <sub>6</sub> H <sub>11</sub>	2.66	0.44	5.22	5.06	-0.36	-1.79	55.2	127.2	112.3	25
<b>E-18c</b> /C <sub>6</sub> H <sub>11</sub>	1.67	1.59	5.77	5.48	2.54	2.22	51.0	131.3	120.4	27
<b>Z-18d</b> /CHMe <sub>2</sub>	2.72	1.15	5.24	4.55	0.30	-1.90	55.2	128.5	110.1	25
<b>E-18d</b> /CHMe <sub>2</sub>	1.70	1.60	5.77	5.48	2.49	2.22	51.3	127.1	110.5	29
<b>Z-18e</b> /CMe <sub>3</sub>	2.54	0.95	5.08	4.54	-0.39	-1.74	55.8	133.9	110.6	24
<b>E-18e</b> /CMe <sub>3</sub>	1.59	1.49	5.78	5.62	2.66	2.44	51.1	132.2	124.2	27

<sup>a</sup>  $^1\text{H}$  (600 MHz) and  $^{13}\text{C}$  (150.8 MHz) NMR spectra recorded in  $[\text{D}_8]\text{toluene}$  at 258 K (**18b** and **18e**), 268 K (**18c**) or 298 K (**18d**). <sup>b</sup> Broad resonances. <sup>c</sup> Second isomer.

**Table 4.** Selected Features of PMMA Formation with Methyl Zirconocene Cation Catalysts **9**<sup>a</sup>

compd	R	conv <sup>b</sup>	mm <sup>c</sup>	mr <sup>c</sup>	rr <sup>c</sup>	$M_w^d$	$D^{d,e}$
<b>9a</b>	H	42	16	24	60	124 000	1.81
<b>9b</b>	CH <sub>3</sub>	47	41	27	32	112 000	2.17
<b>9c</b>	C <sub>6</sub> H <sub>11</sub>	36	64	12	24	64 000	2.32
<b>9d</b>	CHMe <sub>2</sub>	37	87	8	5	30 000	1.10
<b>9e</b>	CMe <sub>3</sub>	53	83	10	7	27 000	1.19
<b>3</b>	f	94	75	13	12	65 000	1.37
<b>11e</b>	g	0 <sup>h</sup>					
<b>13e</b>	g	0 <sup>h</sup>					

<sup>a</sup> Polymerization reaction carried out in  $\text{CH}_2\text{Cl}_2$  at 0 °C, 1 h; in most cases averaged values from several independent experiments are given. <sup>b</sup> Percent monomer conversion after 1 h. <sup>c</sup>  $^1\text{H}$  NMR methyl triad intensities. <sup>d</sup> Molecular weights and polydispersities of the PMMA polymers were obtained by GPC relative to polystyrene standard. <sup>e</sup>  $M_w/M_n$ . <sup>f</sup> See Scheme 1. <sup>g</sup> See Scheme 3. <sup>h</sup> No polymer formation observed during 2 h.

We investigated the MMA polymerization reactions of the isopropyl-substituted catalyst systems **9d** and **18d** in more detail. In each case samples were taken from the polymerization reaction mixtures at ca. 10 min intervals. After quenching, the resulting PMMA samples were analyzed. In each series their stereochemical composition was invariant with time, whereas the molecular weights of the samples linearly increased with increasing monomer conversion, which indicated living polymerization behavior at these catalyst systems. The low polydispersities of the obtained polymer samples ( $M_w/M_n \approx 1.10$ ) are in support of this interpretation. The  $M_n$  vs percent conversion graphs of a pair of representative examples are depicted in Figure 6. Additional data are provided with the Supporting Information.

### The Search for Intermediates

We have tried to get some direct experimental information about reactive intermediates that might be involved in the carbon-carbon coupling reaction of MMA at the *ansa*-zirconocene catalysts. For that purpose the (butadiene)zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  betaine **18a** (R = H) was treated with a ca. 2-fold excess of methyl methacrylate in  $[\text{D}_8]\text{toluene}$  at low temperature under direct NMR control.<sup>36,37</sup> When the temperature was raised from 195 to 253 K, a clean reaction was monitored. The  $\text{Zr}\cdots\text{F}-\text{C}(\text{Ar})$  coordination of **18a** was cleaved,<sup>38</sup> and 1 equiv of methyl methacrylate was coordinated to the catalyst center. This first example of an experimentally observed primary product

(**19a**) in MMA polymerization at a group 4 metallocene catalyst<sup>36</sup> shows the typical NMR features of a Lewis acid activated  $\alpha,\beta$ -unsaturated carbonyl compound. A direct comparison between free MMA, which was present in stoichiometric excess in the solution at 253 K (see Figure 7), revealed that the  $^1\text{H}$  NMR resonances of the coordinated MMA are generally found at smaller  $\delta$  values than the free MMA monomer [free/coordinated MMA:  $\delta$  6.00, 5.07/5.29, 5.04 (=CH<sub>2</sub>),  $\delta$  1.70/1.65 (CH<sub>3</sub>),  $\delta$  3.26/3.11 (OCH<sub>3</sub>)]. The  $^{13}\text{C}$  NMR carbonyl resonance of **19a** appears at  $\delta$  178.4, which is shifted by  $\Delta\delta = 8$  ppm downfield from the corresponding value of the free MMA molecule in the solution ( $\delta$  170.5), which is typical for a strong group 4 metallocene cation coordination to a carbonyl functionality.<sup>39</sup> Likewise, the same effect is observed for the  $^{13}\text{C}$  NMR chemical shift of the MMA Michael position in **19a** ( $\delta$  131.8) vs  $\delta$  126.2 (free MMA). Warming the solution of **19a** above 253 K in the presence of excess methyl methacrylate eventually results in PMMA formation without the observation of further intermediates by NMR.

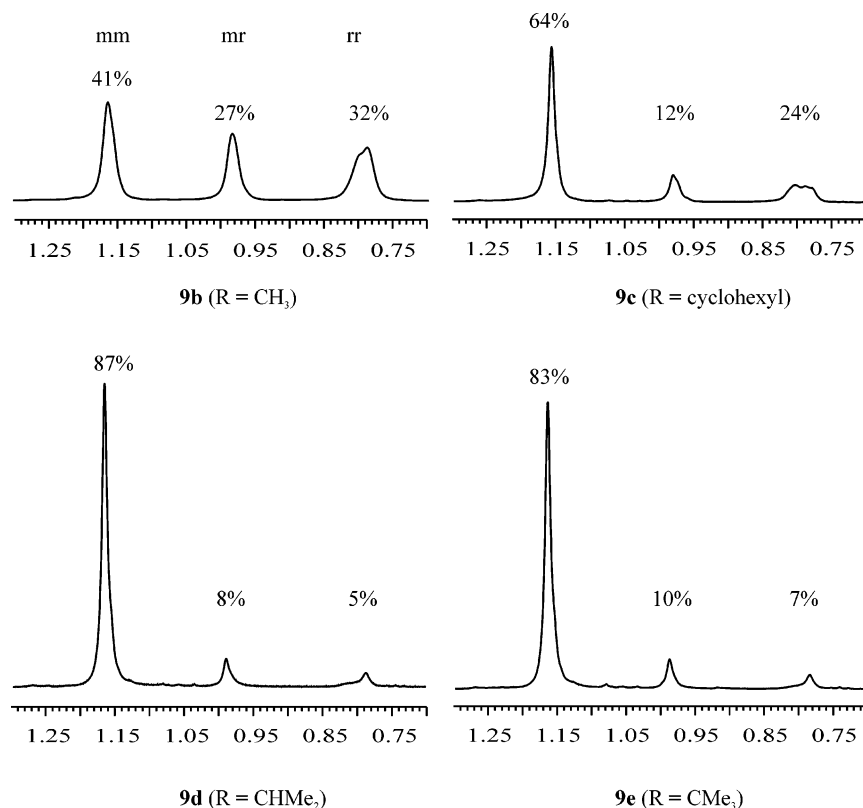
It is possible that we here have observed an initial intermediate of the polymerization reaction. The carbon-carbon coupling sequence would then probably be started by addition of the  $[\text{C}_3\text{H}_4-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]$  moiety to the Michael position of the conjugated carbonyl carbon of **19** to yield the zirconocene enolate system (**20**).<sup>40</sup> This could then sequentially coordinate additional MMA to which enolate addition may occur to build up the PMMA chain at the zirconium center. Eventually a series of neutral oligomeric long chain zirconium-PMMA-enolate complexes would be formed, each carrying a terminal  $[-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3]^-$  anionic moiety (**21**) (see Scheme 9). Hydrolysis of this mixture would then yield a series of oligomeric  $[\text{PMMA}-\text{CH}_2-\text{CH}=\text{CH}_2-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3]^-$  anions (**22**). *The formation of these anions is actually observed.* Treatment of the (butadiene)metallocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  betaine catalyst **18c** (R = cyclohexyl) with MMA for 20 min at 0 °C followed by hydrolysis gave a typical oligomeric distribution of the anions **22** which was analyzed by negative ion electrospray mass spectrometry (ES-MS). Under these conditions we could monitor the appearance of the charged butadiene- $\text{B}(\text{C}_6\text{F}_5)_3$  terminated oligomeric products up to a 20-mer (see Figure 8).<sup>36</sup> A similar oligomeric anion mixture was obtained analogously from MMA coupling at the reference catalyst system **16**. Details are given in the Supporting Information.

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**Figure 4.** Visualization of the pronounced influence of the alkyl groups at the ligand backbone of the catalyst **9** on the isotacticities of the resulting poly(methyl methacrylates) by the relative intensities of the  $^1\text{H}$  NMR methyl triad resonances.

**Table 5.** Characteristic Features of Polymerization Reactions of Methyl Methacrylate with (Butadiene)Zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  Betaine Catalysts **18**<sup>a</sup>

compd	R	conv <sup>b</sup>	mm <sup>c</sup>	mr <sup>c</sup>	rr <sup>c</sup>	$M_w^d$	$D^d$
<b>18a</b>	H	27	15	20	65	58 000	1.70
<b>18b</b>	$\text{CH}_3$	13	26	29	45	44 000	1.22
<b>18c</b>	$\text{C}_6\text{H}_{11}$	22	33	28	39	42 000	1.14
<b>18d</b>	$\text{CHMe}_2$	29	36	24	40	24 000	1.10
<b>18e</b>	$\text{CMe}_3$	20	70	13	17	24 000	1.19
<b>16</b>	e	90	83	10	7	69 000	1.18

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  solution, 1 h, 0 °C; values given are in most cases averaged from several independent experiments. <sup>b</sup> Percent conversion. <sup>c</sup>  $^1\text{H}$  NMR methyl triad intensities. <sup>d</sup> Molecular weights and polydispersities of the PMMA polymers were obtained by GPC relative to polystyrene standard. <sup>e</sup> See Scheme 4.

## Conclusions

It is striking how different the stereochemical outcomes of the polymerization reactions of methyl methacrylate at the [(methyl)zirconocene]<sup>+</sup>[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> systems **9/3** and the (butadiene)zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  betaine catalysts **18/16** are.<sup>35</sup>

Where may these pronounced differences come from? From our observation of the intermediate **19** it is likely that methyl methacrylate coordination to the chiral catalysts is also an essential step in the respective sequence of the polymerization reaction.<sup>41</sup> It may be assumed that MMA coordination from the side of the alkyl substituent creates a situation where the  $\alpha,\beta$ -unsaturated carbonyl compound is effectively shielded from one enantioface (e.g., **24** in Scheme 10) which leads to preferential enolate attack from the other face. Conversely, binding the MMA molecule to the other lateral side of the bent metallocene

wedge (**23** in Scheme 10) might result in a situation where enolate attack could equally readily take place from either enantioface. In contrast to the stereoselective former reaction pathway, the latter situation would probably result in no specific stereocontrol by the chiral *ansa*-metallocene—and thus allow the chiral chain end to govern the overall reaction outcome. Which of the two situations is preferred will, however, not be determined by the relative stabilities of any of the respective rapidly equilibrating ground states (e.g., **23**  $\rightleftharpoons$  **24** in Scheme 10). The stereochemistry will only be determined by the energy differences of the respective transition states of product formation, since this is a typical Curtin–Hammett situation.<sup>42</sup> If we name the equilibrium constant for **23**  $\rightleftharpoons$  **24** as  $K_{\text{eq}}$  (regardless of how equilibration is achieved) and the overall rate constants of the selective/unselective product formation pathways as  $k_1$  and  $k_2$ , then the selective PMMA formation in this typical Curtin–Hammett situation is described by the rate expression (1).

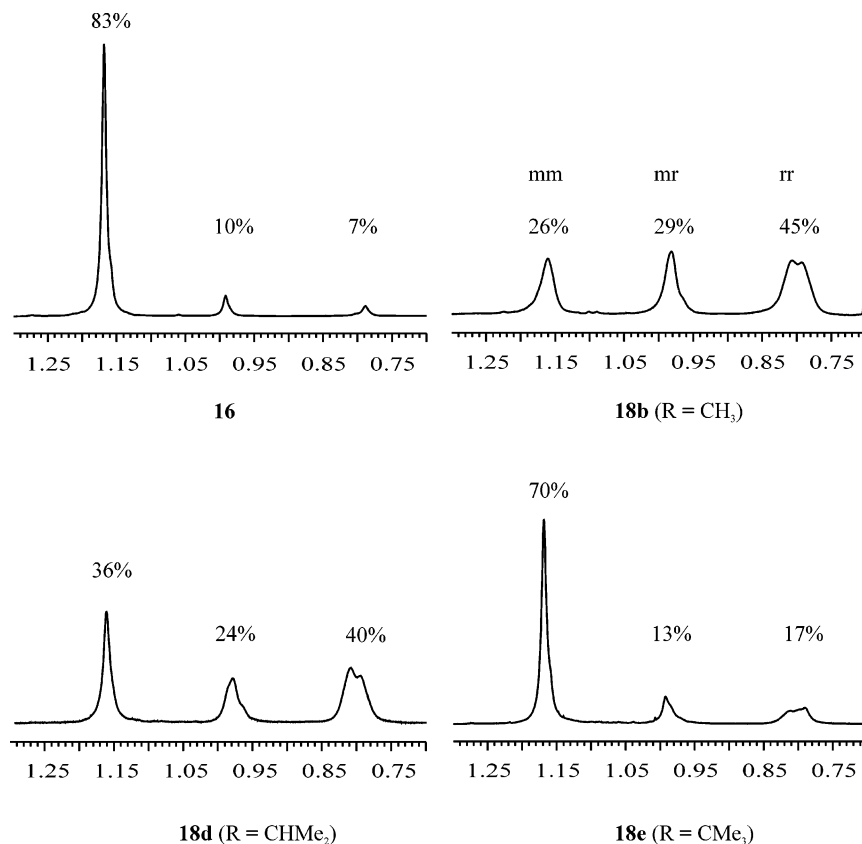
$$\frac{v_1}{v_2} = \frac{k_1}{k_2} K_{\text{eq}} \quad (1)$$

It appears that methyl methacrylate favors coordination from the side where the stereocontrolling alkyl substituent R is located, leaving the less sterically encumbered opposite lateral sector of the metallocene to be occupied by the rather bulky growing polymer chain. As expected, increasing steric bulk of the attached alkyl substituent at the catalyst backbone leads to a more pronounced differentiation of the carbon–carbon bond

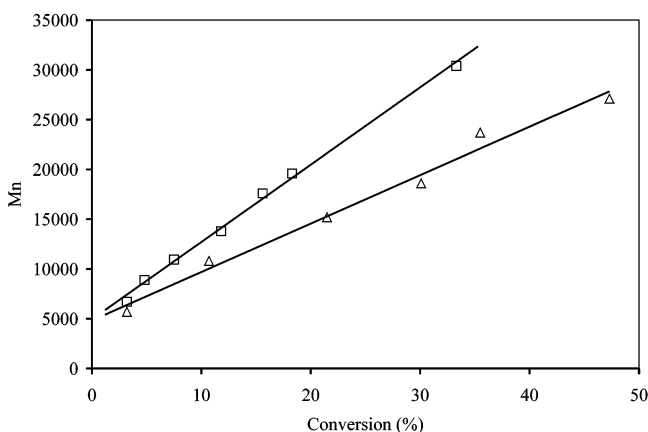
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**Figure 5.**  $^1\text{H}$  NMR methyl triad signals of the poly(methyl methacrylates) obtained with (butadiene)zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  catalysts **18** [ $\text{R} = \text{CH}_3$  (**18b**),  $\text{CHMe}_2$  (**18d**),  $\text{CMe}_3$  (**18e**)] and **16**.



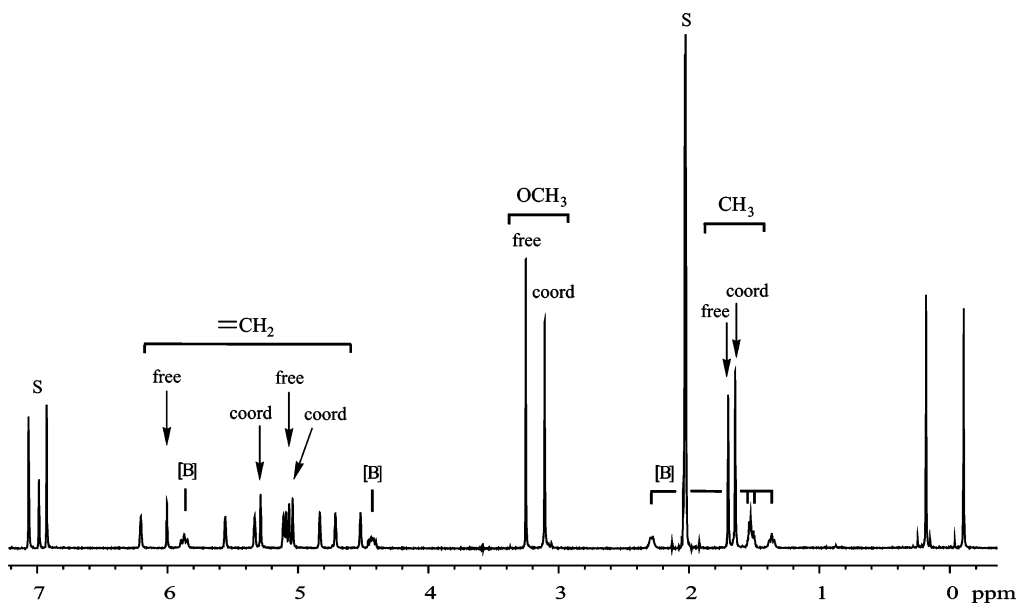
**Figure 6.**  $M_n$  vs % monomer conversion plots for MMA polymerization at the catalyst systems **9d** ( $\Delta$ , linear regression  $r = 0.992$ ), and **18d** ( $\square$ ,  $r = 0.998$ ) at  $0^\circ\text{C}$  in dichloromethane ( $M_n$  by GPC relative to polystyrene standard).

forming transition states and, thus, to an increased enantiomeric site control, which consequently leads to more isotactic poly(methyl methacrylates).

So, why do the two different methods of catalyst formation give rise to such different poly(methyl methacrylates)? It is obvious that two different types of anions are involved. These anions ( $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  associated with the systems **9/3** and the pendent oligomeric  $[\text{PMMA}-\text{C}_4\text{H}_6-\text{B}(\text{C}_6\text{F}_5)_3]^-$  anions at the **18/16** type catalysts that are formed during the initial stages of the living polymerization reactions) probably have quite different ion pairing properties.<sup>23,27</sup> Since the anions cannot kinetically control the actual polymerization process in the Curtin–Hammett situation via their reversible equilibration with the

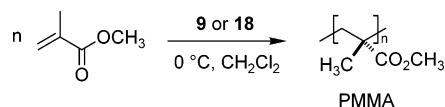
active species, we must assume that the actual active species (e.g., **23/24**) are in fact also ion pairs and that the anions involved here exert a pronounced influence on the respective transition states of the product formation, similar to what has been discussed for anion dependent  $\alpha$ -olefin polymerization at metallocene catalysts.<sup>43–47</sup> Unless the polymerization reactions of the catalyst systems **9** and **18**, respectively, proceed by

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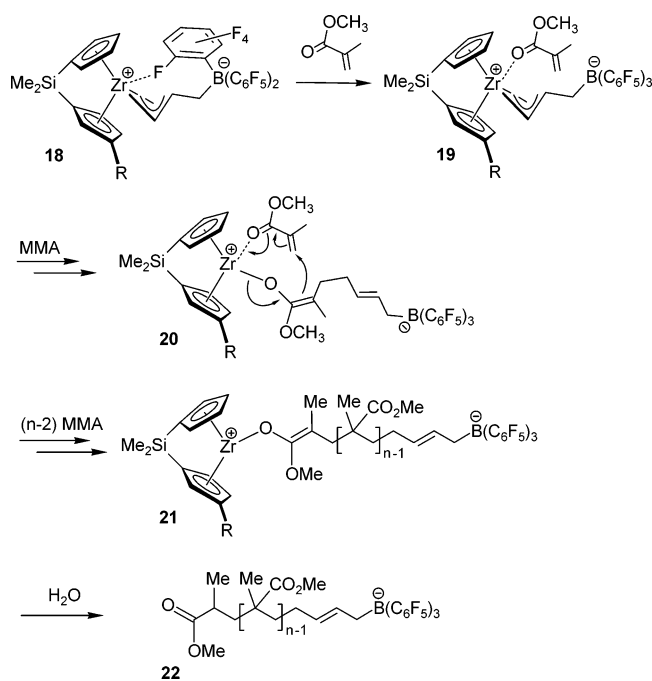


**Figure 7.**  $^1\text{H}$  NMR spectrum (600 MHz, 253 K) of a solution of the intermediate **19a** obtained from the reaction of **18a** with ca. 2-fold amount of methyl methacrylate in  $[\text{D}_8]$ toluene (the signals of free and coordinated MMA are marked, and [B] indicates the signals of the (butadiene)borate fragment).

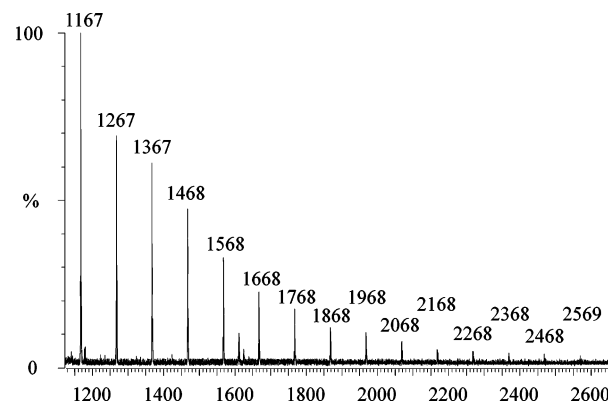
#### Scheme 8



#### Scheme 9

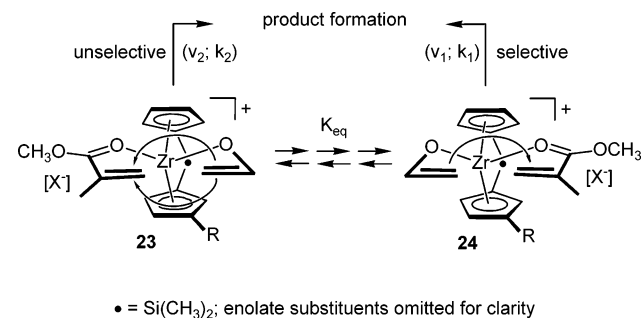


different mechanisms,<sup>48</sup> their observed anion dependent stereochemical performance may add to the cumulating evidence for the involvement of different types of ion pairs in metallocene



**Figure 8.** Negative ion ES-MS of the oligomeric  $[\text{PMMA}-\text{C}_4\text{H}_6-\text{B}(\text{C}_6\text{F}_5)_3]^-$  anion products  $[m/z = 567 + n(100)]$  derived by treatment of the catalyst **18c** with MMA at  $0^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ , followed by hydrolysis.

#### Scheme 10



catalyzed polymerization reactions,<sup>43,45</sup> similar to what is well established in the chemistry of reactive organic carbenium ion systems.<sup>49</sup>

#### Experimental Section

Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general

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information including a list of spectrometers used for physical characterization of the compounds, see ref 29. Lithium cyclopentadienides,<sup>50</sup> indenyllithium,<sup>51</sup> (*cis*-2-buten-1,4-diyl)bis(tetrahydrofuran)-magnesium [“butadiene–magnesium”] (**14**),<sup>26,52</sup> tris(pentafluorophenyl)-borane,<sup>19</sup> bis(pentafluorophenyl)-*N*-pyrrolylborane (**10**),<sup>24</sup> *N*-(2-*H*-pyrrolium)tris(pentafluorophenyl)borate (**12**),<sup>25</sup> (3-alkylcyclopentadienyl)chlorodimethylsilane<sup>21,53</sup> (**4**), (3-alkylcyclopentadienyl)cyclopentadienyldimethylsilane<sup>18,54</sup> (**5**), dilithiobis(alkylcyclopentadienyl)-dimethylsilane<sup>18</sup> (**6**), [dimethylsilylenbis(cyclopentadienyl)]dichlorozirconium (**7a**),<sup>27,54</sup> [dimethylsilylenbis(cyclopentadienyl)]dimethylzirconium<sup>55</sup> (**8a**), {[dimethylsilylenbis(cyclopentadienyl)]methylzirconium} {methyltris(pentafluorophenyl)borate} (**9a**),<sup>13,43</sup> [dimethylsilylenbis(cyclopentadienyl)](butadiene)zirconium (**17a**),<sup>27</sup> [isopropyliden(cyclopentadienyl)(1-indenyl)]dichlorozirconium (**1**),<sup>13,16,56</sup> [isopropyliden(cyclopentadienyl)(1-indenyl)]dimethylzirconium (**2**),<sup>13,15</sup> [isopropyliden(cyclopentadienyl)(1-indenyl)](butadiene)zirconium (**15**),<sup>27</sup> betaine **16**,<sup>27</sup> and betaine **18a**<sup>27</sup> were prepared according to procedures reported in the literature.

**X-ray Crystal Structure Determinations.** Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, M. *Methods Enzymol.* **1997**, 276, 307–326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, A51, 33–37; Blessing, R. H. *J. Appl. Crystallogr.* **1997**, 30, 421–426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997). For further details, see the Supporting Information.

**Generation of [Dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)]dichlorozirconium (7b–e). General Procedure.** Dilithio(3-alkylcyclopentadienyl)(cyclopentadienyl)dimethylsilane (**6b–e**) and tetrachlorobis(tetrahydrofuran)zirconium were mixed as solids in a Schlenk flask. The flask was cooled to  $-78$  °C and toluene was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently the volume of the reaction mixture was reduced to one-third and stored at  $-20$  °C. The obtained precipitate was collected and dried in vacuo.

(**7b**):<sup>27,28</sup> Reaction of **6b** (1.00 g, 4.67 mmol) with tetrachlorobis(tetrahydrofuran)zirconium (1.76 g, 4.67 mmol) in toluene (150 mL) gave 1.12 g (66%, colorless solid) of **7b**. mp 159 °C. Anal. Calcd for  $C_{13}H_{16}SiZrCl_2$  (362.5): C 43.08, H 4.45; found C 42.72, H 4.84. <sup>1</sup>H

NMR (599.9 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 6.87, 6.75, 5.58, 5.35 (each pt, each 1H, C<sub>5</sub>H<sub>4</sub>), 6.44, 5.54, 5.06 (each m, each 1H, MeC<sub>5</sub>H<sub>3</sub>), 2.21 (s, 3H, C<sub>5</sub>H<sub>3</sub>–CH<sub>3</sub>), 0.14, 0.12 (each s, each 3H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (150.8 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 138.9 (ipso-C of MeC<sub>5</sub>H<sub>3</sub>), 128.2, 115.5, 114.0 (MeC<sub>5</sub>H<sub>3</sub>), 127.9, 127.1, 114.2, 113.0 (C<sub>5</sub>H<sub>4</sub>), 107.6 (ipso-C of MeC<sub>5</sub>H<sub>3</sub>Si), 107.5 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 15.5 (C<sub>5</sub>H<sub>3</sub>–CH<sub>3</sub>), –5.6, –6.0 (Si(CH<sub>3</sub>)<sub>2</sub>).

(**7c**): Reaction of **6c** (2.96 g, 10.3 mmol) with tetrachlorobis(tetrahydrofuran)zirconium (3.88 g, 10.3 mmol) in toluene (80 mL) gave 2.59 g (58%, light orange solid) of **7c**. mp 172 °C. Anal. Calcd for  $C_{13}H_{16}SiZrCl_2$  (362.5): C 50.21, H 5.62; found C 49.33, H 6.02. <sup>1</sup>H NMR (599.9 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 6.83, 6.81, 5.55, 5.47 (each pt, each 1H, C<sub>5</sub>H<sub>4</sub>), 6.69, 5.54, 5.30 (each pt, each 1H, cyC<sub>5</sub>H<sub>3</sub>), 2.99 (m, 1H, CH of cy), 2.32, 1.89, 1.70, 1.67, 1.60, 1.43, 1.38, 1.32, 1.14, 1.06 (each m, each 1H, CH<sub>2</sub> of cy), 0.18, 0.11 (each s, each 3H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (150.8 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 147.8 (ipso-C of cyC<sub>5</sub>H<sub>3</sub>), 128.9, 126.5, 114.2, 113.1 (C<sub>5</sub>H<sub>4</sub>), 126.6, 113.9, 112.8 (cyC<sub>5</sub>H<sub>3</sub>), 107.6 (ipso-C of cyC<sub>5</sub>H<sub>3</sub>Si), 107.3 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 38.6 (CH of cy), 35.9, 31.8, 26.9, 26.5, 26.4 (CH<sub>2</sub> of cy), –5.5, –6.0 (Si(CH<sub>3</sub>)<sub>2</sub>).

(**7d**): Reaction of **6d** (1.00 g, 4.13 mmol) with tetrachlorobis(tetrahydrofuran)zirconium (1.56 g, 4.13 mmol) in toluene (50 mL) gave 0.96 g (60%, light brown solid) of **7d**. mp 162 °C. Anal. Calcd for  $C_{15}H_{20}SiZrCl_2$  (390.5): C 46.13, H 5.16; found C 46.04, H 5.49. <sup>1</sup>H NMR (599.9 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 6.83, 6.80, 5.54, 5.45 (each pt, each 1H, C<sub>5</sub>H<sub>4</sub>), 6.67, 5.53, 5.29 (each m, each 1H, <sup>i</sup>PrC<sub>5</sub>H<sub>3</sub>), 3.29 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>i</sup>Pr–CH), 1.32, 1.09 (each d, each 3H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>i</sup>Pr–CH<sub>3</sub>), 0.17, 0.09 (each s, each 3H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (150.8 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 148.8 (ipso-C of <sup>i</sup>PrC<sub>5</sub>H<sub>3</sub>), 128.8, 126.6, 114.3, 112.9 (C<sub>5</sub>H<sub>4</sub>), 126.4, 113.9, 113.1 (<sup>i</sup>PrC<sub>5</sub>H<sub>3</sub>), 107.7 (ipso-C of <sup>i</sup>PrC<sub>5</sub>H<sub>3</sub>Si), 107.5 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 29.0 (<sup>i</sup>Pr–CH), 24.8, 21.4 (<sup>i</sup>Pr–CH<sub>3</sub>), –5.5, –6.0 (Si(CH<sub>3</sub>)<sub>2</sub>).

(**7e**): Reaction of **6e** (2.50 g, 9.75 mmol) with tetrachlorobis(tetrahydrofuran)zirconium (3.68 g, 9.75 mmol) in toluene (70 mL) gave 2.54 g (64%, light yellow solid) of **7e**. mp 165 °C. Anal. Calcd for  $C_{16}H_{22}SiZrCl_2$  (404.6): C 47.50, H 5.48; found C 47.22, H 5.82. <sup>1</sup>H NMR (599.9 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 6.84, 6.65, 5.65, 5.45 (each pt, each 1H, C<sub>5</sub>H<sub>4</sub>), 6.82, 5.7, 5.54 (each m, each 1H, <sup>t</sup>BuC<sub>5</sub>H<sub>3</sub>), 1.42 (s, 9H, <sup>t</sup>Bu–CH<sub>3</sub>), 0.22, 0.09 (each s, each 3H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (150.8 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 150.4 (ipso-C of <sup>t</sup>BuC<sub>5</sub>H<sub>3</sub>), 130.9, 124.9, 117.5, 111.4 (C<sub>5</sub>H<sub>4</sub>), 129.5, 113.8, 113.7 (<sup>t</sup>BuC<sub>5</sub>H<sub>3</sub>), 107.9 (ipso-C of <sup>t</sup>BuC<sub>5</sub>H<sub>3</sub>Si), 105.7 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 33.7 (C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (<sup>t</sup>Bu–CH<sub>3</sub>), –4.5, –6.6 (Si(CH<sub>3</sub>)<sub>2</sub>).

**Generation of [Dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)]dimethylzirconium (8b–e). General Procedure.** A solution of methylolithium in ether was added dropwise to a solution of the dichlorozirconocene complex **7** in toluene or diethyl ether at  $-78$  °C. After 30 min the reaction mixture was allowed to warm to room temperature and stirred for a further 3 h. Subsequently the reaction mixture was filtered and the residue was washed twice with 10 mL of pentane. The product **8** was obtained as a solid after removing the solvent from the filtrate in vacuo.

(**8b**): Reaction of **7b** (0.30 g, 0.83 mmol) in toluene (30 mL) with methylolithium in ether (1.85 M, 0.89 mL, 1.66 mmol) gave 0.19 g (70%, light yellow solid) of **8b**. Anal. Calcd for  $C_{15}H_{22}SiZr$  (321.5): C 56.01, H 6.89; found C 55.75, H 6.80. <sup>1</sup>H NMR (599.9 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 6.74, 6.70, 5.49, 5.34 (each pt, each 1H, C<sub>5</sub>H<sub>4</sub>), 6.37, 5.39, 5.08 (each m, each 1H, MeC<sub>5</sub>H<sub>3</sub>), 2.16 (s, 3H, C<sub>5</sub>H<sub>3</sub>–CH<sub>3</sub>), 0.15, 0.14 (each s, each 3H, Si(CH<sub>3</sub>)<sub>2</sub>), –0.08, –0.16 (each s, each 3H, Zr(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (150.8 MHz, [D<sub>6</sub>]benzene, 298 K):  $\delta$  = 130.1 (ipso-C of MeC<sub>5</sub>H<sub>3</sub>), 121.4, 112.9, 112.6 (MeC<sub>5</sub>H<sub>3</sub>), 120.4, 120.3, 112.4, 112.0 (C<sub>5</sub>H<sub>4</sub>), 100.2 (ipso-C of MeC<sub>5</sub>H<sub>3</sub>Si), 100.1 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 32.7, 29.0 (Zr(CH<sub>3</sub>)<sub>2</sub>), 14.8 (C<sub>5</sub>H<sub>3</sub>–CH<sub>3</sub>), –5.3, –5.5 (Si(CH<sub>3</sub>)<sub>2</sub>).

(**8c**): Reaction of **7c** (0.50 g, 1.16 mmol) in diethyl ether (20 mL) with methylolithium in ether (1.90 M, 1.22 mL, 2.32 mmol) was carried out as described above. After stirring for 2 h at room temperature the

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diethyl ether solvent was changed for toluene (20 mL). The reaction mixture was filtered, the obtained solid was washed with toluene (5 mL) twice, and the solvent from the filtrate was removed in vacuo. The obtained crude product was stirred in pentane (20 mL) at  $-78\text{ }^{\circ}\text{C}$ , collected by filtration, and dried in vacuo to yield 0.30 g (67%, light brown solid) of **8c**. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{SiZr}$  (389.8): C 61.63, H 7.76; found C 61.33, H 7.98.  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.75, 6.71, 5.45, 5.44$  (each pt, each 1H,  $\text{C}_5\text{H}_4$ ), 6.59, 5.38, 5.28 (each pt, each 1H,  $\text{cyC}_5\text{H}_3$ ), 2.71 (m, 1H,  $\text{CH}_2$  of cy), 2.12, 1.98, 1.72, 1.71, 1.63, 1.47, 1.38, 1.36, 1.31, 1.15 (each m, each 1H,  $\text{CH}_2$  of cy), 0.19, 0.14 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ),  $-0.03, 0.12$  (each s, each 3H,  $\text{Zr}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 140.7$  (ipso-C of  $\text{cyC}_5\text{H}_3$ ), 121.3, 120.0, 112.8, 111.4 ( $\text{C}_5\text{H}_4$ ), 118.8, 111.6, 110.9 ( $\text{cyC}_5\text{H}_3$ ), 100.3 (ipso-C of  $\text{cyC}_5\text{H}_3\text{Si}$ ), 99.7 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 38.5 ( $\text{CH}$  of cy), 36.4, 32.8, 27.0, 26.7, 26.5 ( $\text{CH}_2$  of cy), 32.1, 28.9 ( $\text{Zr}(\text{CH}_3)_2$ ),  $-5.1, -5.7$  ( $\text{Si}(\text{CH}_3)_2$ ).

**(8d):** Reaction of **7d** (0.30 g, 0.77 mmol) in toluene (30 mL) with methyl lithium in ether (1.85 M, 0.83 mL, 1.54 mmol) gave 0.20 g (75%, light yellow solid) of **8d**. Anal. Calcd for  $\text{C}_{17}\text{H}_{26}\text{SiZr}$  (349.7): C 58.39, H 7.49; found C 58.40, H 7.56.  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.74, 6.70, 5.44, 5.42$  (each pt, each 1H,  $\text{C}_5\text{H}_4$ ), 6.57, 5.36, 5.27 (each m, each 1H,  $^i\text{PrC}_5\text{H}_3$ ), 3.00 (sept, 1H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr}-\text{CH}$ ), 1.28, 1.20 (each d, each 3H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr}-\text{CH}_3$ ), 0.18, 0.12 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ),  $-0.05, -0.13$  (each s, each 3H,  $\text{Zr}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 141.7$  (ipso-C of  $^i\text{PrC}_5\text{H}_3$ ), 121.3, 120.0, 112.7, 111.5 ( $\text{C}_5\text{H}_4$ ), 118.6, 111.7, 110.8 ( $^i\text{PrC}_5\text{H}_3$ ), 100.3 (ipso-C of  $^i\text{PrC}_5\text{H}_3\text{Si}$ ), 99.8 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 32.1, 28.8 ( $\text{Zr}(\text{CH}_3)_2$ ), 28.6 ( $^i\text{Pr}-\text{CH}$ ), 25.3, 22.4 ( $^i\text{Pr}-\text{CH}_3$ ),  $-5.1, -5.7$  ( $\text{Si}(\text{CH}_3)_2$ ).

**(8e):** Reaction of **7e** (0.50 g, 1.24 mmol) in diethyl ether (20 mL) with methyl lithium in ether (1.83 M, 1.35 mL, 2.47 mmol) was carried out as described above. After stirring for 2 h at room temperature the solvent was changed to toluene (20 mL). The reaction mixture was filtered, the obtained solid was washed with toluene (5 mL) twice, and the solvent was removed from the combined filtrates in vacuo. The obtained crude product was stirred in pentane (20 mL) at  $-78\text{ }^{\circ}\text{C}$ , collected by filtration, and dried in vacuo to yield 0.32 g (71%, light yellow solid) of **8e**. Anal. Calcd for  $\text{C}_{18}\text{H}_{28}\text{SiZr}$  (363.7): C 59.44, H 7.76; found C 60.10, H 7.65.  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.74, 6.56, 5.58, 5.36$  (each pt, each 1H,  $\text{C}_5\text{H}_4$ ), 6.67, 5.62, 5.32 (each pt, each 1H,  $^t\text{BuC}_5\text{H}_3$ ), 1.37 (s, 1H,  $^t\text{Bu}-\text{CH}_3$ ), 0.21, 0.12 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ), 0.01, 0.00 (each s, each 3H,  $\text{Zr}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 145.1$  (ipso-C of  $^t\text{BuC}_5\text{H}_3$ ), 122.2, 119.6, 114.4, 110.4 ( $\text{C}_5\text{H}_4$ ), 120.1, 111.9, 110.2 ( $^t\text{BuC}_5\text{H}_3$ ), 100.5 (ipso-C of  $^t\text{BuC}_5\text{H}_3\text{Si}$ ), 98.6 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 31.6, 28.2 ( $\text{Zr}(\text{CH}_3)_2$ ), 33.4 ( $\text{C}(\text{CH}_3)_2$ ), 31.3 ( $^t\text{Bu}-\text{CH}_3$ ),  $-4.3, -6.1$  ( $\text{Si}(\text{CH}_3)_2$ ).

**In Situ Generation of  $\{[\text{Isopropylidene}(\text{cyclopentadienyl})-(1\text{-indenyl})\text{methylzirconium}]\{\text{Methyltris}(\text{pentafluorophenyl})\text{borate}\}$  (**3**).** Two separate solutions were prepared, one of [isopropylidene(cyclopentadienyl)(1-indenyl)]dimethylzirconium (**2**) (16 mg, 46  $\mu\text{mol}$ ) in  $[\text{D}_2]$ dichloromethane (0.5 mL), and one of tris(pentafluorophenyl)borane (24 mg, 46  $\mu\text{mol}$ ) in  $[\text{D}_2]$ dichloromethane (0.5 mL). Subsequently the borane solution was added dropwise to the zirconocene solution. The obtained reaction mixture was directly characterized by NMR. A 4:1 mixture of the two regioisomeric ion pairs was obtained.

**(3) Major Isomer:**  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_2]$ dichloromethane, 253 K):  $\delta = 7.66$  (m, 1H, 4-H), 7.52 (m, 1H, 7-H), 7.47 (m, 1H, 5-H), 7.10 (m, 1H, 6-H), 6.85 (m, 1H, 5'-H), 6.52 (pd, 1H, 3-H), 6.27 (pd, 1H, 2-H), 6.17, 5.81 (each m, each 1H, 3' and 4'-H), 5.52 (m, 1H, 2'-H), 1.99 (s, 3H,  $\text{C}(\text{CH}_3)_2\text{-syn}$ ), 1.89 (s, 3H,  $\text{C}(\text{CH}_3)_2\text{-anti}$ ),  $-0.75$  (s, 3H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_2]$ dichloromethane, 253 K):  $\delta = 129.5$  (C3a), 127.5 (C5,  $^1J_{\text{CH}} = 163$  Hz), 127.0 (C6,  $^1J_{\text{CH}} = 160$  Hz), 126.4 (C4,  $^1J_{\text{CH}} = 163$  Hz), 126.1 (C7,  $^1J_{\text{CH}} = 164$  Hz), 119.8 (C5',  $^1J_{\text{CH}} = 178$  Hz and C7a), 115.8 (C1'), 115.3 (C4',  $^1J_{\text{CH}} = 173$  Hz), 113.2 (C2,  $^1J_{\text{CH}} = 168$  Hz), 108.6 (C2',  $^1J_{\text{CH}} = 173$  Hz), 105.5

(C3,  $^1J_{\text{CH}} = 176$  Hz), 104.2 (C3',  $^1J_{\text{CH}} = 170$  Hz), 100.0 (C1), 42.7 ( $\text{Zr}-\text{CH}_3$ ,  $^1J_{\text{CH}} = 123$  Hz), 39.3 ( $\text{C}(\text{CH}_3)_2$ ), 25.8 ( $\text{C}(\text{CH}_3)_2\text{-anti}$ ), 24.6 ( $\text{C}(\text{CH}_3)_2\text{-syn}$ ).

**(3) Minor Isomer:**  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_2]$ dichloromethane, 253 K):  $\delta = 7.62$  (m, 2H, 4-H, 7-H), 7.32 (m, 1H, 2-H), 6.81 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.73 (pt, 1H, 6-H), 6.48 (pt, 1H, 5-H), 5.87 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.80 (m, 2H, 3-H,  $\text{C}_5\text{H}_4'$ ), 5.43 (m, 1H,  $\text{C}_5\text{H}_4'$ ), 2.07 (s, 3H,  $\text{C}(\text{CH}_3)_2\text{-anti}$ ), 1.78 (s, 3H,  $\text{C}(\text{CH}_3)_2\text{-syn}$ ), 0.66 (s, 3H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.9 MHz,  $[\text{D}_2]$ dichloromethane, 253 K):  $\delta = 128.4$  (C3a), 126.8 (C6), 125.7, (C5), 124.8, 121.7 (C4, C7), 121.0 ( $\text{C}_5\text{H}_4'$ ), 118.3 (7a), 116.8 (C1'), 114.9 (C3), 113.4 ( $\text{C}_5\text{H}_4'$ ), 112.3 (C2), 108.5 ( $\text{C}_5\text{H}_4'$ ), 104.0 ( $\text{C}_5\text{H}_4'$ ), 99.4 (C1), 44.7 ( $\text{Zr}-\text{CH}_3$ ), 39.1 ( $\text{C}(\text{CH}_3)_2$ ), 25.9 ( $\text{C}(\text{CH}_3)_2\text{-anti}$ ), 24.8 ( $\text{C}(\text{CH}_3)_2\text{-syn}$ ).

**In Situ Generation of  $\{[\text{Dimethylsilylen}(3\text{-alkylcyclopentadienyl})-(\text{cyclopentadienyl})\text{methylzirconium}]\{\text{Methyltris}(\text{pentafluorophenyl})\text{borate}\}$  (**9b-e**),  $\{[\text{Dimethylsilylen}(3\text{-tert-butylcyclopentadienyl})-(\text{cyclopentadienyl})\text{methylzirconium}]\{\text{Methylbis}(\text{pentafluorophenyl})\text{-}N\text{-pyrrolylborate}\}$  (*anti/syn-11e*), and  $\{[\text{Dimethylsilylen}(3\text{-tert-butylcyclopentadienyl})(\text{cyclopentadienyl})\text{methylzirconium}]\{\text{Tris}(\text{pentafluorophenyl})\text{-}N\text{-pyrrolylborate}\}$  (*anti/syn-13e*).** General Procedure. Two separate solutions were prepared, one of [dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)]dimethylzirconium (**8b-d**) in  $[\text{D}_6]$ benzene (0.5 mL), and one of the borane in  $[\text{D}_6]$ benzene (0.5 mL). Subsequently the borane solution was added dropwise to the zirconocene solution. The obtained golden (**8**) or orange (**11**, **13**) reaction mixture was directly characterized by NMR experiments.

**(9b)** was generated by the reaction of **8b** (20 mg, 62  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (32 mg, 63  $\mu\text{mol}$ ).  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.44, 6.25, 5.37, 4.80$  (each m, each 1H,  $\text{C}_5\text{H}_4$ ), 6.00, 5.31, 4.57 (each m, each 1H,  $\text{MeC}_6\text{F}_5$ ), 1.85 (s, 3H,  $\text{C}_5\text{H}_3-\text{CH}_3$ ), 0.90 (br s, 3H,  $(\text{CH}_3)\text{B}(\text{C}_6\text{F}_5)_3$ ), 0.23 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.02,  $-0.18$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 149.2$  (dm,  $^1J_{\text{CF}} = 245$  Hz, *o*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 138.3 (dm,  $^1J_{\text{CF}} = 235$  Hz, *p*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 137.4 (dm,  $^1J_{\text{CF}} = 245$  Hz, *m*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 136.4 (ipso-C of  $\text{MeC}_5\text{H}_3$ ), 128.2 (br, ipso-B( $\text{C}_6\text{F}_5$ )), 124.8, 121.9, 117.6, 111.5 ( $\text{C}_5\text{H}_4$ ), 122.3, 118.2, 112.4 ( $\text{MeC}_5\text{H}_3$ ), 105.1, 104.9 (ipso-C of  $\text{MeC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 42.1 ( $\text{Zr}-\text{CH}_3$ ), 14.3 ( $\text{C}_5\text{H}_3-\text{CH}_3$ ),  $-5.9, -6.6$  ( $\text{Si}(\text{CH}_3)_2$ ). ( $\text{Me}-[\text{B}]$  was not observed).

**(9c)** was generated by the reaction of **8c** (22 mg, 56  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (29 mg, 56  $\mu\text{mol}$ ).  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.42, 6.34, 5.33, 4.90$  (each pt, each 1H,  $\text{C}_5\text{H}_4$ ), 6.30, 5.40, 4.84 (each pt, each 1H,  $\text{cyC}_5\text{H}_3$ ), 2.45 (m, 1H,  $\text{CH}$  of cy), 1.68, 1.66, 1.57, 1.54, 1.48, 1.21, 1.18, 1.13, 0.98, 0.95 (each m, each 1H,  $\text{CH}_2$  of cy), 0.54 (br, 3H,  $(\text{CH}_3)\text{B}(\text{C}_6\text{F}_5)_3$ ), 0.32 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.04,  $-0.19$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 149.4$  (dm,  $^1J_{\text{CF}} = 235$  Hz, *o*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 139.0 (dm,  $^1J_{\text{CF}} = 245$  Hz, *p*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 137.9 (dm,  $^1J_{\text{CF}} = 245$  Hz, *m*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 146.8 (ipso-C of  $\text{cyC}_5\text{H}_3$ ), 128.6 (ipso-B( $\text{C}_6\text{F}_5$ )), 124.2, 122.6, 118.0, 110.8 ( $\text{C}_5\text{H}_4$ ), 119.8, 116.4, 111.0 ( $\text{cyC}_5\text{H}_3$ ), 105.3, 104.8 (ipso-C of  $\text{cyC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 40.8 ( $\text{Zr}-\text{CH}_3$ ), 38.2 ( $\text{CH}$  of cy), 36.0, 31.6, 26.5, 26.0, 25.8 ( $\text{CH}_2$  of cy),  $-5.6, -6.9$  ( $\text{Si}(\text{CH}_3)_2$ ). ( $\text{Me}-[\text{B}]$  was not observed).

**(9d)** was generated by the reaction of **8d** (20 mg, 57  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (29 mg, 57  $\mu\text{mol}$ ).  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 6.43, 6.30, 5.36, 4.82$  (each m, each 1H,  $\text{C}_5\text{H}_4$ ), 6.23, 5.38, 4.78 (each m, each 1H,  $^i\text{PrC}_5\text{H}_3$ ), 2.66 (sept, 1H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^i\text{Pr}-\text{CH}$ ), 0.90, 0.88 (each d, each 3H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^i\text{Pr}-\text{CH}_3$ ), 0.50 (br s, 3H,  $(\text{CH}_3)\text{B}(\text{C}_6\text{F}_5)_3$ ), 0.29 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.02,  $-0.21$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta = 148.7$  (dm,  $^1J_{\text{CF}} = 240$  Hz, *o*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 148.2 (ipso-C of  $^i\text{PrC}_5\text{H}_3$ ), 138.0 (dm,  $^1J_{\text{CF}} = 240$  Hz, *p*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 136.4 (dm,  $^1J_{\text{CF}} = 235$  Hz, *m*- $\text{B}(\text{C}_6\text{F}_5)_3$ ), 129.2 (br, ipso-B( $\text{C}_6\text{F}_5$ )), 124.9, 122.2, 117.6, 112.2 ( $\text{C}_5\text{H}_4$ ), 119.3, 115.9, 111.4 ( $^i\text{PrC}_5\text{H}_3$ ), 105.3, 105.1 (ipso-C of  $^i\text{PrC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 42.1 ( $\text{Zr}-\text{CH}_3$ ), 28.5 ( $^i\text{Pr}-\text{CH}$ ), 24.8, 20.5 ( $^i\text{Pr}-\text{CH}_3$ )  $-5.8, -6.8$  ( $\text{Si}(\text{CH}_3)_2$ ). ( $\text{Me}-[\text{B}]$  was not observed).

(**9e**) was generated by the reaction of **8e** (21 mg, 58  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (30 mg, 58  $\mu\text{mol}$ ).  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 6.40, 5.37, 5.27 (each pt, each 1H,  $^1\text{BuC}_5\text{H}_3$ ), 6.33, 6.29, 5.20, 5.07 (each d, each 1H,  $\text{C}_5\text{H}_4$ ), 0.98 (s, 9H,  $^1\text{Bu}-\text{CH}_3$ ), 0.57 (br s, 3H,  $(\text{CH}_3)_3\text{B}(\text{C}_6\text{F}_5)_3$ ), 0.46 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.03,  $-0.24$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 151.4 (ipso-C of  $^1\text{BuC}_5\text{H}_3$ ), 148.6 (dm,  $^1J_{\text{CF}}$  = 240 Hz,  $o\text{-B}(\text{C}_6\text{F}_5)_3$ ), 137.6 (dm,  $^1J_{\text{CF}}$  = 250 Hz,  $p\text{-B}(\text{C}_6\text{F}_5)_3$ ), 136.4 (dm,  $^1J_{\text{CF}}$  = 245 Hz,  $m\text{-B}(\text{C}_6\text{F}_5)_3$ ), 128.3 (br, ipso-B( $\text{C}_6\text{F}_5$ ) $_3$ ), 123.3, 123.2, 119.7, 109.7 ( $\text{C}_5\text{H}_4$ ), 121.4, 115.9, 111.1 ( $^1\text{BuC}_5\text{H}_3$ ), 105.3, 103.6 (ipso-C of  $^1\text{BuC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 42.1 ( $\text{Zr}-\text{CH}_3$ ), 33.6 ( $\text{C}(\text{CH}_3)_3$ ), 30.5 ( $^1\text{Bu}-\text{CH}_3$ ),  $\sim 21$  (br,  $(\text{CH}_3)_3\text{B}(\text{C}_6\text{F}_5)_3$ ),  $-4.9$ ,  $-7.4$  ( $\text{Si}(\text{CH}_3)_2$ ).

(**11e**) was generated by reaction of **8e** (20 mg, 55  $\mu\text{mol}$ ) with bis(pentafluorophenyl)-*N*-pyrrolylborane (23 mg, 55  $\mu\text{mol}$ ). Two isomers were obtained: *anti*-**11e**:*syn*-**11e** = 3:1.

**anti-11e**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 7.40, 7.32 (each d, each 1H,  $^3J_{\text{HH}}$  = 1.8 Hz,  $\alpha$ -pyrrole), 6.29, 4.77 (each pt, each 1H,  $\text{C}_5\text{H}_4$ ), 5.97, 5.10, 5.03 (each pt, each 1H,  $^1\text{BuC}_5\text{H}_3$ ), 5.91, 5.44 (each d, each 1H,  $^3J_{\text{HH}}$  = 1.8 Hz,  $\beta$ -pyrrole), 4.95 (m, 2H,  $\text{C}_5\text{H}_4$ ), 1.18 (br s, 3H,  $(\text{CH}_3)_3\text{B}(\text{NC}_4\text{H}_4)(\text{C}_6\text{F}_5)_2$ ), 1.13 (s, 9H,  $^1\text{Bu}-\text{CH}_3$ ), 0.13 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.10,  $-0.15$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 150.1 (ipso-C of  $^1\text{BuC}_5\text{H}_3$ ), 148.7 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $o\text{-B}(\text{C}_6\text{F}_5)_3$ ), 140.3, 136.3 ( $\alpha$ -pyrrole), 137.7 (dm,  $^1J_{\text{CF}}$  = 250 Hz,  $p\text{-B}(\text{C}_6\text{F}_5)_3$ ), 137.4 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $m\text{-B}(\text{C}_6\text{F}_5)_3$ ), 129.0 (ipso-B( $\text{C}_6\text{F}_5$ ) $_3$ ), 127.1, 124.1, 114.9, 109.0 ( $\text{C}_5\text{H}_4$ ), 121.1, 112.6, 109.1 ( $^1\text{BuC}_5\text{H}_3$ ), 103.8, 97.5 ( $\beta$ -pyrrole), 102.7, 100.8 (ipso-C of  $^1\text{BuC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 38.6 ( $\text{Zr}-\text{CH}_3$ ), 32.6 ( $\text{C}(\text{CH}_3)_3$ ), 30.9 ( $^1\text{Bu}-\text{CH}_3$ ),  $\sim 11$  (br,  $(\text{CH}_3)_3\text{B}(\text{NC}_4\text{H}_4)(\text{C}_6\text{F}_5)_2$ ),  $-5.3$ ,  $-7.0$  ( $\text{Si}(\text{CH}_3)_2$ ).

**syn-11e**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 7.48, 7.46 (each d, each 1H,  $^3J_{\text{HH}}$  = 1.8 Hz,  $\alpha$ -pyrrole), 6.03, 5.92 (each d, each 1H,  $\text{C}_5\text{H}_4$ ), 5.97, 5.13, 4.98, 4.85 (each m, each 1H,  $\text{C}_5\text{H}_4$ ), 5.94, 5.38, 5.07 (each pt, each 1H,  $^1\text{BuC}_5\text{H}_3$ ), 1.23 (br s, 3H,  $(\text{CH}_3)_3\text{B}(\text{NC}_4\text{H}_4)(\text{C}_6\text{F}_5)_2$ ), 0.98 (s, 9H,  $^1\text{Bu}-\text{CH}_3$ ), 0.31 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.23, 0.16 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 150.3 (ipso-C of  $^1\text{BuC}_5\text{H}_3$ ), 148.7 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $o\text{-B}(\text{C}_6\text{F}_5)_3$ ), 140.3, 136.3 ( $\alpha$ -pyrrole), 137.7 (dm,  $^1J_{\text{CF}}$  = 250 Hz,  $p\text{-B}(\text{C}_6\text{F}_5)_3$ ), 137.3 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $m\text{-B}(\text{C}_6\text{F}_5)_3$ ), 129.0 (br, ipso-B( $\text{C}_6\text{F}_5$ ) $_3$ ), 125.8, 121.1, 118.1, 112.5 ( $\text{C}_5\text{H}_4$ ), 120.8, 112.7, 109.8 ( $^1\text{BuC}_5\text{H}_3$ ), 105.1, 104.7 (ipso-C of  $^1\text{BuC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 101.8, 98.3 ( $\beta$ -pyrrole), 34.0 ( $\text{Zr}-\text{CH}_3$ ), 33.7 ( $\text{C}(\text{CH}_3)_3$ ), 29.9 ( $^1\text{Bu}-\text{CH}_3$ ),  $\sim 11$  (br,  $(\text{CH}_3)_3\text{B}(\text{NC}_4\text{H}_4)(\text{C}_6\text{F}_5)_2$ ),  $-5.9$ ,  $-6.1$  ( $\text{Si}(\text{CH}_3)_2$ ).

(**13e**) was generated by reaction of **8e** (20 mg, 55  $\mu\text{mol}$ ) with *N*-(2*H*-pyrrolyl) tris(pentafluorophenyl)borate (32 mg, 55  $\mu\text{mol}$ ). Two isomers were formed: *anti*-**13e**:*syn*-**13e** = 4:1.

**anti-13e**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 7.21, 7.18 (each br, each 1H,  $\alpha$ -pyrrole), 6.55, 5.46, 5.28, 4.86 (each m, each 1H,  $\text{C}_5\text{H}_4$ ), 6.12, 5.31, 5.05 (each pt, each 1H,  $^1\text{BuC}_5\text{H}_3$ ), 5.83, 5.35 (each d, each 1H,  $^3J_{\text{HH}}$  = 1.8 Hz,  $\beta$ -pyrrole), 1.10 (s, 9H,  $^1\text{Bu}-\text{CH}_3$ ), 0.23 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.21,  $-0.10$  (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 155.4 (ipso-C of  $^1\text{BuC}_5\text{H}_3$ ), 148.6 (dm,  $^1J_{\text{CF}}$  = 245 Hz,  $o\text{-B}(\text{C}_6\text{F}_5)_3$ ), 148.1 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $p\text{-B}(\text{C}_6\text{F}_5)_3$ ), 139.1, 136.9 ( $\alpha$ -pyrrole), 137.6 (dm,  $^1J_{\text{CF}}$  = 250 Hz,  $m\text{-B}(\text{C}_6\text{F}_5)_3$ ), 128.2 (ipso-B( $\text{C}_6\text{F}_5$ ) $_3$ ), 125.9, 124.3, 115.8, 112.7 ( $\text{C}_5\text{H}_4$ ), 120.5, 112.3, 111.4 ( $^1\text{BuC}_5\text{H}_3$ ), 105.5, 98.9 ( $\beta$ -pyrrole), 103.0, 101.6 (ipso-C of  $^1\text{BuC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 41.3 ( $\text{Zr}-\text{CH}_3$ ), 32.7 ( $\text{C}(\text{CH}_3)_3$ ), 30.7 ( $^1\text{Bu}-\text{CH}_3$ ),  $-5.6$ ,  $-6.8$  ( $\text{Si}(\text{CH}_3)_2$ ).

**syn-13e**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 7.37, 7.27 (each br, each 1H,  $\alpha$ -pyrrole), 6.09, 5.81 (each m, each 1H,  $\beta$ -pyrrole), 6.07, 5.47, 5.24 (each pt, each 1H,  $^1\text{BuC}_5\text{H}_3$ ), 5.82, 5.71, 5.25, 5.22 (each m, each 1H,  $\text{C}_5\text{H}_4$ ), 0.97 (s, 9H,  $^1\text{Bu}-\text{CH}_3$ ), 0.37 (s, 3H,  $\text{Zr}-\text{CH}_3$ ), 0.23, 0.15 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_6]$ benzene, 298 K):  $\delta$  = 151.6 (ipso-C of  $^1\text{BuC}_5\text{H}_3$ ), 148.6 (dm,  $^1J_{\text{CF}}$  = 245 Hz,  $o\text{-B}(\text{C}_6\text{F}_5)_3$ ), 148.1 (dm,  $^1J_{\text{CF}}$  = 235 Hz,  $p\text{-B}(\text{C}_6\text{F}_5)_3$ ), 140.9, 139.4 ( $\alpha$ -pyrrole), 137.6 (dm,  $^1J_{\text{CF}}$  = 250 Hz,

$m\text{-B}(\text{C}_6\text{F}_5)_3$ ), 123.1, 121.4, 103.0, 101.6 ( $\text{C}_5\text{H}_4$ ), 119.9, 113.1, 109.6 ( $^1\text{BuC}_5\text{H}_3$ ), 113.5, 113.2 (ipso-C of  $^1\text{BuC}_5\text{H}_3\text{Si}$  and ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 102.7, 98.3 ( $\beta$ -pyrrole), 34.0 ( $\text{Zr}-\text{CH}_3$ ), 30.4 ( $\text{C}(\text{CH}_3)_3$ ), 29.8 ( $^1\text{Bu}-\text{CH}_3$ ),  $-5.7$ ,  $-6.5$  ( $\text{Si}(\text{CH}_3)_2$ ).

**Syntheses of the [Dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)](butadiene)zirconium Complexes (*s-cis*-**17b**-*e/s-cis*-**17b**-*e*, *s-trans*-**17b**-*e/s-trans*-**17b**-*e*). **General Procedure.** The respective dichlorozirconocene complex **7** and 1.1 mol equiv of the butadiene–magnesium reagent were mixed as solids in a Schlenk flask. The flask was cooled to  $-78$   $^\circ\text{C}$ , and precooled toluene (20 mL) was added slowly. During a time period of 6 h the reaction mixture was allowed to warm to room temperature, and the system was stirred for additional 6 h. After filtration and washing of the residue with toluene (5 mL, twice), the volume of the filtrate was reduced to one-third. Subsequently, the solution was stored at  $-20$   $^\circ\text{C}$ . The product precipitated as a powder, which was collected, washed with cold pentane (5 mL), and dried in vacuo.**

(**17b**):<sup>27,28</sup> Reaction of **7b** (500 mg, 1.40 mmol) with “butadiene–magnesium” (326 mg, 1.46 mmol) gave 330 mg (68%, red-brown solid) of **17b**. *s-cis*:*s-trans* = 95:5 (*s-cis*-**17b**:*s-cis*-**17b** = 4:1; *s-trans*-**17b**:*s-trans*-**17b** = 5:1). Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{SiZr}$  (345.7): C 59.07, H 6.42; found C 59.64, H 5.82.

**s-cis-17b**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 5.92 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 5.42 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 5.19 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.98 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.91 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.79 (q,  $^3J_{\text{HH}}$  = 11.8 Hz, 1H, 3-H), 4.69 (q,  $^3J_{\text{HH}}$  = 11.8 Hz, 1H, 2-H), 4.21 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 3.37 (m, 1H,  $4_{\text{syn}}\text{-H}$ ), 3.36 (m, 1H,  $1_{\text{syn}}\text{-H}$ ), 1.70 (s, 3H,  $\text{C}_5\text{H}_3\text{-CH}_3$ ), 0.42 (s, 3H, 6-H), 0.29 (s, 3H, 5-H),  $-0.76$  (dd, 1H,  $^3J_{\text{HH}}$  = 11.8 Hz,  $^2J_{\text{HH}}$  = 9.2 Hz,  $1_{\text{anti}}\text{-H}$ ),  $-1.50$  (dd, 1H,  $^3J_{\text{HH}}$  = 11.8 Hz,  $^2J_{\text{HH}}$  = 8.4 Hz,  $4_{\text{anti}}\text{-H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 142.8 (ipso-C of  $\text{MeC}_5\text{H}_3$ ), 112.4 (C3), 110.1 (C2), 109.9 ( $\text{C}_5\text{H}_4$ ), 109.0 ( $\text{C}_5\text{H}_4$ ), 109.0 ( $\text{MeC}_5\text{H}_3$ ), 103.2 ( $\text{C}_5\text{H}_4$ ), 102.9 (ipso-C of  $\text{MeC}_5\text{H}_3\text{Si}$ ), 101.2 ( $\text{MeC}_5\text{H}_3$ ), 100.8 ( $\text{C}_5\text{H}_4$ ), 99.9 ( $\text{MeC}_5\text{H}_3$ ), 93.2 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 54.1 (C4), 49.5 (C1), 14.7 ( $\text{C}_5\text{H}_3\text{-CH}_3$ ),  $-3.6$  (C6),  $-6.5$  (C5).

**s-cis-17b**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 5.48 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.41 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 5.22 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.98 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 4.80 (m, 1H, 3-H), 4.71 (m, 1H, 2-H), 4.56 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.25 (m, 1H,  $\text{C}_5\text{H}_4$ ), 3.75 (m, 1H,  $\text{MeC}_5\text{H}_3$ ), 3.43 (m, 1H,  $1_{\text{syn}}\text{-H}$ ), 3.12 (m, 1H,  $4_{\text{syn}}\text{-H}$ ), 1.26 (s, 3H,  $\text{C}_5\text{H}_3\text{-CH}_3$ ), 0.41 (s, 3H, 6-H), 0.28 (s, 3H, 5-H),  $-0.83$  (m, 1H,  $1_{\text{anti}}\text{-H}$ ),  $-0.88$  (m, 1H,  $4_{\text{anti}}\text{-H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 130.0 (ipso-C of  $\text{MeC}_5\text{H}_3$ ), 112.7 (C3), 112.0 (C2), 111.2 ( $\text{C}_5\text{H}_4$ ), 111.0 ( $\text{C}_5\text{H}_4$ ), 109.2 ( $\text{MeC}_5\text{H}_3$ ), 102.4 (ipso-C of  $\text{MeC}_5\text{H}_3\text{Si}$ ), 97.3 ( $\text{MeC}_5\text{H}_3$ ), 96.4 ( $\text{MeC}_5\text{H}_3$ ), 95.5 ( $\text{C}_5\text{H}_4$ ), 95.0 ( $\text{C}_5\text{H}_4$ ), 94.0 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 51.9 (C4), 50.6 (C1), 13.8 ( $\text{C}_5\text{H}_3\text{-CH}_3$ ),  $-4.8$  (C6),  $-6.0$  (C5).

**s-trans-17b (Major s-trans Isomer)**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 5.97, 5.66, 5.62, 5.04, 4.89, 4.74, 4.48 (each m, each 1H,  $\text{MeC}_5\text{H}_3$ ,  $\text{C}_5\text{H}_4$ ), 3.08 (dd, 1H,  $^3J_{\text{HH}}$  = 6.6 Hz,  $^2J_{\text{HH}}$  = 3.6 Hz,  $\text{H}_{\text{syn}}$ ), 2.89 (dt, 1H,  $^3J_{\text{HH}}$  = 15.6 Hz,  $^3J_{\text{HH}}$  = 6.6 Hz,  $\text{H}_{\text{meso}}$ ), 2.61 (dd, 1H,  $^3J_{\text{HH}}$  = 6.6 Hz,  $^2J_{\text{HH}}$  = 3.2 Hz,  $\text{H}_{\text{syn}}$ ), 2.35 (dt, 1H,  $^3J_{\text{HH}}$  = 15.6 Hz,  $^3J_{\text{HH}}$  = 6.6 Hz,  $\text{H}_{\text{meso}}$ ), 1.30 (dd, 1H,  $^3J_{\text{HH}}$  = 15.6 Hz,  $^2J_{\text{HH}}$  = 3.2 Hz,  $\text{H}_{\text{anti}}$ ), 1.23 (dd, 1H,  $^3J_{\text{HH}}$  = 15.6 Hz,  $^2J_{\text{HH}}$  = 3.6 Hz,  $\text{H}_{\text{anti}}$ ), 1.48 (s, 3H,  $\text{C}_5\text{H}_3\text{-CH}_3$ ), 0.31, 0.29 (each s, each 3H,  $\text{Si}(\text{CH}_3)_2$ ).

**s-trans-17b**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]$ toluene, 268 K):  $\delta$  = 3.16 (dd, 1H,  $^3J_{\text{HH}}$  = 7.2 Hz,  $^2J_{\text{HH}}$  = 4.2 Hz,  $\text{H}_{\text{syn}}$ ), 2.90 (dt, 1H,  $^3J_{\text{HH}}$  = 16.0 Hz,  $^3J_{\text{HH}}$  = 7.2 Hz,  $\text{H}_{\text{meso}}$ ), 2.77 (m, 1H,  $\text{H}_{\text{syn}}$ ), 2.55 (dt, 1H,  $^3J_{\text{HH}}$  = 16.0 Hz,  $^2J_{\text{HH}}$  = 7.2 Hz,  $\text{H}_{\text{meso}}$ ), 1.33, 1.29 (each m, each 1H,  $\text{H}_{\text{anti}}$ ). (Due to the low concentration of this isomer in the mixture, no further resonances were identified.)

(**17c**): Reaction of **7c** (500 mg, 1.15 mmol) with “butadiene–magnesium” (270 mg, 1.21 mmol) gave 304 mg (63%, red-brown solid) of **17c**. *s-cis*:*s-trans* > 98:2 (*s-cis*-**17c**:*s-cis*-**17c** = 4:1). Anal. Calcd for  $\text{C}_{22}\text{H}_{30}\text{SiZr}$  (413.8): C 63.86, H 7.31; found C 64.57, H 6.85.

**s-cis-17c**:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]$ toluene, 228 K):  $\delta$  = 6.02 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.60 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.28 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.92 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.86 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.76 (m, 1H, 3-H), 4.66 (m, 1H, 2-H),

4.02 (pt, 1H,  $\text{cyC}_5\text{H}_3$ ), 3.44 (t, 1H,  $^3J_{\text{HH}} = ^2J_{\text{HH}} = 9.6$  Hz,  $4_{\text{syn-H}}$ ), 3.35 (t, 1H,  $^3J_{\text{HH}} = ^2J_{\text{HH}} = 9.6$  Hz,  $1_{\text{syn-H}}$ ), 3.21 (m, 1H, CH of cy), 1.80–1.00 (10H,  $\text{CH}_2$  of cy), 0.48 (s, 3H, 6-H), 0.30 (s, 3H, 5-H),  $-0.73$  (t, 1H,  $^2J_{\text{HH}} = 9.6$  Hz,  $1_{\text{anti-H}}$ ),  $-1.45$  (dd, 1H,  $^3J_{\text{HH}} = 12.1$  Hz,  $^2J_{\text{HH}} = 9.6$  Hz,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 228 K):  $\delta = 143.4$  (ipso-C of  $\text{cyC}_5\text{H}_3$ ), 112.7 (C3), 110.4 ( $\text{C}_5\text{H}_4$ ), 109.2 (C2), 109.1 ( $\text{C}_5\text{H}_4$ ), 105.2 ( $\text{cyC}_5\text{H}_3$ ), 102.8 ( $\text{cyC}_5\text{H}_3$ ), 102.0 ( $\text{C}_5\text{H}_4$ ), 101.4 (ipso-C of  $\text{cyC}_5\text{H}_3\text{Si}$ ), 99.8 ( $\text{C}_5\text{H}_4$ ), 96.3 ( $\text{cyC}_5\text{H}_3$ ), 95.4 (ipso-C of  $\text{C}_5\text{H}_4\text{-Si}$ ), 60.8 (CH of cy), 54.1 (C4), 50.1 (C1), 38.2, 36.7, 32.5, 26.9, 26.6 ( $\text{CH}_2$  of cy),  $-3.2$  (C6),  $-6.7$  (C5).

***s-cis-17'c***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 6.07$  (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.93 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.69 (dd, 1H,  $\text{C}_5\text{H}_4$ ), 5.53 (m, 1H,  $\text{cyC}_5\text{H}_3$ ), 5.16 (m, 1H,  $\text{cyC}_5\text{H}_3$ ), 4.83 (m, 1H, 3-H), 4.70 (m, 1H, 2-H), 4.17 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 1H,  $\text{cyC}_5\text{H}_3$ ), 3.46 (m, 1H,  $4_{\text{syn-H}}$ ), 3.22 (t, 1H,  $^3J_{\text{HH}} = ^2J_{\text{HH}} = 9.2$  Hz,  $1_{\text{syn-H}}$ ), 2.61 (m, 1H, CH of cy), 1.80–1.00 (10H,  $\text{CH}_2$  of cy), 0.49 (6-H), 0.29 (5-H),  $-0.77$  (dd, 1H,  $^3J_{\text{HH}} = 11.8$  Hz,  $^2J_{\text{HH}} = 9.2$  Hz,  $1_{\text{anti-H}}$ ),  $-0.88$  (dd, 1H,  $^3J_{\text{HH}} = 12.3$  Hz,  $^2J_{\text{HH}} = 9.4$  Hz,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 137.6$  (ipso-C of  $\text{cyC}_5\text{H}_3$ ), 118.6 ( $\text{C}_5\text{H}_4$ ), 112.1 (C3), 111.6 (C2), 108.6 ( $\text{cyC}_5\text{H}_3$ ), 104.9 ( $\text{C}_5\text{H}_4$ ), 104.5 ( $\text{C}_5\text{H}_4$ ), 99.7 (ipso-C of  $\text{cyC}_5\text{H}_3\text{-Si}$ ), 99.1 ( $\text{C}_5\text{H}_4$ ), 95.5 ( $\text{cyC}_5\text{H}_3$ ), 94.5 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 94.1 ( $\text{cyC}_5\text{H}_3$ ), 61.1 (CH of cy), 52.3 (C4), 50.7 (C1), 37.7, 32.1, 26.7, 26.5, 26.4 ( $\text{CH}_2$  of cy),  $-3.0$  (C6),  $-6.8$  (C5).

***s-trans-17c***: Due to the low concentration of the trans isomers, only the resonances of the butadiene fragments were clearly assigned.  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 3.26$ , 3.03, 2.85, 2.78.

**(17d)**: Reaction of **7d** (500 mg, 1.28 mmol) with “butadiene–magnesium” (302 mg, 1.36 mmol) gave 304 mg (63%, red-brown solid) of **17d**. *s-cis:s-trans*  $\approx 97:3$  (*s-cis-17d:s-cis-17'd* = 3:1; *s-trans-17d:s-trans-17'd* = 5:1). Anal. Calcd for  $\text{C}_{19}\text{H}_{26}\text{SiZr}$  (373.7): C 61.13, H 6.97; found C 61.50, H 7.08.

***s-cis-17d***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 5.99$  (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 5.61 (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 5.25 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.92 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.88 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.78 (q, 1H, 3-H), 4.66 (q,  $^3J_{\text{HH}} = 10.9$  Hz, 1H, 2-H), 4.10 (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 3.40 (m, 1H,  $4_{\text{syn-H}}$ ), 3.36 (m, 1H,  $1_{\text{syn-H}}$ ), 2.10 (sept, 1H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr-CH}$ ), 1.22, 0.90 (each d, each 3H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr-CH}_3$ ), 0.43 (s, 3H, 6-H), 0.30 (s, 3H, 5-H),  $-0.78$  (dd, 1H,  $^3J_{\text{HH}} = 12.3$  Hz,  $^2J_{\text{HH}} = 8.8$  Hz,  $1_{\text{anti-H}}$ ),  $-1.45$  (dd, 1H,  $^3J_{\text{HH}} = 12.4$  Hz,  $^2J_{\text{HH}} = 8.4$  Hz,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 143.1$  (ipso-C of  $^i\text{PrC}_5\text{H}_3$ ), 112.7 (C3), 110.4 ( $\text{C}_5\text{H}_4$ ), 109.8 (C2), 109.1 ( $\text{C}_5\text{H}_4$ ), 105.9 ( $^i\text{PrC}_5\text{H}_3$ ), 102.7 ( $^i\text{PrC}_5\text{H}_3$ ), 102.3 ( $\text{C}_5\text{H}_4$ ), 101.4 (ipso-C of  $^i\text{PrC}_5\text{H}_3\text{Si}$ ), 100.1 ( $\text{C}_5\text{H}_4$ ), 96.1 ( $^i\text{PrC}_5\text{H}_3$ ), 94.1 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 54.0 (C4), 50.1 (C1), 28.3 ( $^i\text{Pr-CH}$ ), 25.6, 22.1 (each  $^i\text{Pr-CH}_3$ ),  $-3.2$  (C6),  $-6.6$  (C5).

***s-cis-17'd***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 6.04$  (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.89 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.67 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.28 (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 4.87 (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 4.83 (m, 1H, 3-H), 4.79 (m, 1H, 2-H), 4.77 (m, 1H,  $^i\text{PrC}_5\text{H}_3$ ), 4.24 (m, 1H,  $\text{C}_5\text{H}_4$ ), 3.41 (t, 1H,  $^2J_{\text{HH}} = ^3J_{\text{HH}} = 11.2$  Hz,  $1_{\text{syn-H}}$ ), 3.20 (t, 1H,  $^2J_{\text{HH}} = ^3J_{\text{HH}} = 9.6$  Hz,  $4_{\text{syn-H}}$ ), 1.87 (sept, 1H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr-CH}$ ), 1.02, 0.86 (each d, each 3H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^i\text{Pr-CH}_3$ ), 0.44 (s, 3H, 6-H), 0.29 (s, 3H, 5-H),  $-0.79$  (m, 1H,  $1_{\text{anti-H}}$ ),  $-0.91$  (dd,  $^3J_{\text{HH}} = 8.9$  Hz,  $^2J_{\text{HH}} = 9.6$  Hz, 1H,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 130.4$  (ipso-C of  $^i\text{PrC}_5\text{H}_3$ ), 118.5 ( $\text{C}_5\text{H}_4$ ), 112.3 (C3), 111.5 ( $^i\text{PrC}_5\text{H}_3$ ), 111.2 (C2), 105.4 ( $^i\text{PrC}_5\text{H}_3$ ), 105.0 ( $\text{C}_5\text{H}_4$ ), 104.5 ( $\text{C}_5\text{H}_4$ ), 101.3 (ipso-C of  $^i\text{PrC}_5\text{H}_3\text{Si}$ ), 99.0 ( $\text{C}_5\text{H}_4$ ), 98.7 ( $^i\text{PrC}_5\text{H}_3$ ), 93.8 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 52.5 (C4), 50.6 (C1), 28.2 ( $^i\text{Pr-CH}$ ), 26.5, 21.9 ( $^i\text{Pr-CH}_3$ ),  $-3.1$  (C6),  $-6.7$  (C5).

Due to the low concentration of the trans isomers, only the resonances of the butadiene derived ligand section are listed.

***s-trans-17d (Major Isomer)***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 3.16$  (dd, 1H,  $^3J_{\text{HH}} = 7.0$  Hz,  $^2J_{\text{HH}} = 4.0$  Hz,  $\text{H}_{\text{syn}}$ ), 2.88 (dt, 1H,  $^3J_{\text{HH}} = 11.9$  Hz,  $^3J_{\text{HH}} = 6.5$  Hz,  $\text{H}_{\text{meso}}$ ), 2.61 (dd, 1H,  $^3J_{\text{HH}} = 6.5$  Hz,  $^2J_{\text{HH}} = 3.7$  Hz,  $\text{H}_{\text{syn}}$ ), 2.55 (dt, 1H,  $^3J_{\text{HH}} = 11.9$  Hz,  $^3J_{\text{HH}} = 4.0$  Hz,  $\text{H}_{\text{meso}}$ ), 1.38 (m, 1H,  $\text{H}_{\text{anti}}$ ), 1.23 (m, 1H,  $\text{H}_{\text{anti}}$ ).

***s-trans-17d***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 248 K):  $\delta = 3.24$  (dd, 1H,  $^3J_{\text{HH}} = 6.4$  Hz,  $^2J_{\text{HH}} = 3.0$  Hz,  $\text{H}_{\text{syn}}$ ), 3.30 (dt, 1H,  $^3J_{\text{HH}} =$

11.9 Hz,  $^3J_{\text{HH}} = 6.4$  Hz,  $\text{H}_{\text{meso}}$ ), 2.97 (dd, 1H,  $^3J_{\text{HH}} = 6.6$  Hz,  $^2J_{\text{HH}} = 3.0$  Hz,  $\text{H}_{\text{syn}}$ ), 2.68 (dpt, 1H,  $^3J_{\text{HH}} = 11.9$  Hz,  $^2J_{\text{HH}} = 6.6$  Hz,  $\text{H}_{\text{meso}}$ ), 1.43, 1.32 (each m, each 1H,  $\text{H}_{\text{anti}}$ ).

**(17e)**: reaction of **7e** (500 mg, 1.24 mmol) with “butadiene–magnesium” (292 mg, 1.31 mmol) gave 352 mg (73%, red-brown solid) of **17e**. *s-cis:s-trans*  $> 99:1$  (*s-cis-17e:s-cis-17'e* = 1:1). Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{SiZr}$  (387.8): C 61.95, H 7.28; found C 62.02, H 7.20.

***s-cis-17e***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 5.99$  (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 5.65 (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 5.31 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.99 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.89 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.81 (dd, 1H,  $\text{C}_5\text{H}_4$ ), 4.73 (q, 1H,  $^3J_{\text{HH}} = 13.1$  Hz, 3-H), 4.62 (q, 1H,  $^3J_{\text{HH}} = 13.1$  Hz, 2-H), 4.41 (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 3.42 (dd, 1H,  $^3J_{\text{HH}} = 13.1$ ,  $^2J_{\text{HH}} = 9.0$  Hz,  $1_{\text{syn-H}}$ ), 3.27 (dd, 1H,  $^3J_{\text{HH}} = 13.1$  Hz,  $^2J_{\text{HH}} = 9.0$  Hz,  $4_{\text{syn-H}}$ ), 1.09 (s, 9H,  $^3J_{\text{HH}} = ^i\text{Bu-CH}_3$ ), 0.44 (s, 3H, 6-H), 0.29 (s, 3H, 5-H),  $-0.72$  (dd, 1H,  $^3J_{\text{HH}} = 13.1$  Hz,  $^2J_{\text{HH}} = 9.0$  Hz,  $1_{\text{anti-H}}$ ),  $-0.86$  (dd, 1H,  $^3J_{\text{HH}} = 13.1$  Hz,  $^2J_{\text{HH}} = 9.0$  Hz,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 148.0$  (ipso-C of  $^i\text{BuC}_5\text{H}_3$ ), 112.1 (C3), 110.9 ( $\text{C}_5\text{H}_4$ ), 110.1 (C2), 108.9 ( $\text{C}_5\text{H}_4$ ), 103.9 ( $^i\text{BuC}_5\text{H}_3$ ), 103.3 ( $^i\text{BuC}_5\text{H}_3$ ), 101.7 ( $\text{C}_5\text{H}_4$ ), 101.1 (ipso-C of  $^i\text{BuC}_5\text{H}_3\text{Si}$ ), 99.1 ( $\text{C}_5\text{H}_4$ ), 97.3 ( $^i\text{BuC}_5\text{H}_3$ ), 95.3 (ipso-C of  $\text{C}_5\text{H}_4\text{Si}$ ), 51.6 (C4), 51.4 (C1), 32.6 ( $\text{C}(\text{CH}_3)_3$ ), 32.1 ( $^i\text{Bu-CH}_3$ ),  $-3.1$  (C6),  $-6.6$  (C5).

***s-cis-17'e***:  $^1\text{H}$  NMR (599.9 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 6.19$  (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.10 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.72 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.32 (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 5.14 (q, 1H,  $^3J_{\text{HH}} = 13.0$  Hz, 3-H), 4.90 (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 4.68 (pt, 1H,  $^i\text{BuC}_5\text{H}_3$ ), 4.67 (q, 1H,  $^3J_{\text{HH}} = 13.0$  Hz, 2-H), 4.00 (m, 1H,  $\text{C}_5\text{H}_4$ ), 3.47 (m, 1H,  $4_{\text{syn-H}}$ ), 3.25 (m, 1H,  $1_{\text{syn-H}}$ ), 0.96 (s, 9H,  $^3J_{\text{HH}} = ^i\text{Bu-CH}_3$ ), 0.47 (s, 3H, 6-H), 0.28 (s, 3H, 5-H),  $-0.70$  (dd, 1H,  $^3J_{\text{HH}} = 13.0$  Hz,  $^2J_{\text{HH}} = 8.2$  Hz,  $1_{\text{anti-H}}$ ),  $-0.96$  (ddd, 1H,  $^3J_{\text{HH}} = 13.0$  Hz,  $^2J_{\text{HH}} = 7.8$  Hz,  $4_{\text{anti-H}}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150.8 MHz,  $[\text{D}_8]\text{toluene}$ , 253 K):  $\delta = 135.2$  (ipso-C of  $^i\text{BuC}_5\text{H}_3$ ), 117.6 ( $\text{C}_5\text{H}_4$ ), 113.4 (C3), 110.7 ( $\text{C}_5\text{H}_4$ ), 109.1 (C2), 109.0 ( $^i\text{BuC}_5\text{H}_3$ ), 106.1 ( $^i\text{BuC}_5\text{H}_3$ ), 102.8 ( $\text{C}_5\text{H}_4$ ), 101.4 ( $\text{C}_5\text{H}_4$ ), 99.9 (ipso-C of  $^i\text{BuC}_5\text{H}_3\text{Si}$ ), 98.8 (ipso-C of  $\text{C}_5\text{H}_4\text{-Si}$ ), 96.5 ( $^i\text{BuC}_5\text{H}_3$ ), 52.1 (C4), 50.3 (C1), 31.6 ( $\text{C}(\text{CH}_3)_3$ ), 31.4 ( $^i\text{Bu-CH}_3$ ),  $-2.2$  (C6),  $-6.9$  (C5).

**Addition of Tris(pentafluorophenyl)borane to the (Butadiene)-zirconocenes 17b–e. General Procedure for the Preparation of Betaines 18b–e.** Two separate solutions were prepared, one of [dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)](butadiene)-zirconium (**17b–d**) in toluene (5 mL), and one of the borane  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene (5 mL). At  $-78$  °C the borane solution was added dropwise to the (butadiene)zirconocene solution. Then the reaction mixture was allowed to warm to room temperature. After stirring for further 2 h all volatiles were removed in vacuo. The residue was suspended in pentane (10 mL) and stirred for 30 min at  $-78$  °C. Then the precipitate was collected, washed with pentane (5 mL), and dried in vacuo.

**(18b)**:<sup>27</sup> Reaction of **17b** (100 mg, 289  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (148 mg, 289  $\mu\text{mol}$ ) gave 196 mg (79%, light brown solid) of **18b**. Anal. Calcd for  $\text{C}_{35}\text{H}_{22}\text{SiBF}_{15}\text{Zr}$  (857.6): C 50.18, H 2.96; found C 50.61, H 2.87.

**(18c)**: Reaction of **17c** (140 mg, 338  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (175 mg, 338  $\mu\text{mol}$ ) gave 258 mg (83%, light brown solid) of **18c**. Anal. Calcd for  $\text{C}_{40}\text{H}_{30}\text{SiBF}_{15}\text{Zr}$  (925.7): C 51.90, H 3.27; found C 52.05, H 4.13.

**(18d)**: Reaction of **17d** (100 mg, 268  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (137 mg, 268  $\mu\text{mol}$ ) gave 165 mg (69%, light brown solid) of **18d**. Anal. Calcd for  $\text{C}_{37}\text{H}_{26}\text{SiBF}_{15}\text{Zr}$  (885.7): C 49.02, H 2.96; found C 48.82, H 3.41.

**(18e)**: Reaction of **17e** (100 mg, 258  $\mu\text{mol}$ ) with tris(pentafluorophenyl)borane (132 mg, 258  $\mu\text{mol}$ ) gave 206 mg (88%, light yellow solid) of **18e**. Anal. Calcd for  $\text{C}_{38}\text{H}_{28}\text{SiBF}_{15}\text{Zr}$  (899.7): C 50.73, H 3.14; found C 50.24, H 3.89.

**In Situ Addition of Tris(pentafluorophenyl)borane to the (Butadiene)zirconocenes 17b–e. General Procedure for the Preparation of Betaines 18b–e for NMR Experiments.** Two separate solutions were prepared, one of [dimethylsilylen(3-alkylcyclopentadienyl)(cyclopentadienyl)](butadiene)zirconium (**17b–d**) in  $[\text{D}_8]\text{toluene}$  (0.8 mL),

and one of the borane  $B(C_6F_5)_3$  in  $[D_8]$ toluene (0.4 mL). Subsequently the borane solution was added dropwise to the (butadiene)zirconocene solution. The **Z-18** isomers were observed as kinetic products.

**(18b):** Reaction of **17b** (20 mg, 57.9  $\mu$ mol) with tris(pentafluorophenyl)borane (29.6 mg, 57.9  $\mu$ mol) gave **18b** as a mixture of isomers (*E-18b*:*E-18'b* = 4:1).

**Z-18b:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 5.82 (pt, 1H,  $MeC_5H_3$ ), 5.38, 5.29 (each m, each 1H,  $C_5H_4$ ), 5.16 (m, 1H, 2-H), 4.91 (m, 1H,  $C_5H_4$ ), 4.74, 4.55 (each pt, each 1H,  $MeC_5H_3$ ), 4.49 (t, 1H,  $^3J_{HH} = 11.8$  Hz, 3-H), 4.23 (m, 1H,  $C_5H_4$ ), 2.62 (t, 1H,  $^3J_{HH} = 13.4$  Hz,  $1_{syn-H}$ ), 1.53 (s, 3H,  $C_5H_3-CH_3$ ), 0.27 (m, 1H,  $1_{anti-H}$ ), 0.11, 0.08 (each s, each 3H,  $Si(CH_3)_2$ ), -0.43 (br, 1H, 4'-H), -1.83 (br, 1H, 4-H).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 146.0 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ), 138.9 (dm,  $^1J_{CF} = 250$  Hz, *p*- $B(C_6F_5)_3$ ), 137.6 (dm,  $^1J_{CF} = 250$  Hz, *m*- $B(C_6F_5)_3$ ), 136.6 (ipso-C of  $MeC_5H_3$ ), 131.4 (C2), 117.9 (C3), 117.6 ( $MeC_5H_3$ ), 114.5 ( $C_5H_4$ ), 114.1 ( $MeC_5H_3$ ), 113.2 ( $C_5H_4$ ), 112.5, 109.2 ( $C_5H_4$ ), 103.2 ( $MeC_5H_3$ ), 101.5 (ipso-C of  $MeC_5H_3Si$ ), 99.6 (ipso-C of  $C_5H_4Si$ ), 55.0 (C1), 25 (br, C4), 14.5 ( $C_5H_3-CH_3$ ), -5.8, -8.1 ( $Si(CH_3)_2$ ).

**E-18b (Major E Isomer):**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 5.97 (m, 1H,  $C_5H_4$ ), 5.91 (m, 1H, 2-H), 5.72 (m, 1H,  $C_5H_4$ ), 5.58 (m, 1H,  $MeC_5H_3$ ), 5.51 (m, 1H,  $C_5H_4$ ), 5.17 (m, 1H,  $MeC_5H_3$ ), 4.69 (m, 1H, 3-H), 4.35 (pt, 1H,  $MeC_5H_3$ ), 4.23 (m, 1H,  $C_5H_4$ ), 2.50 (br d, 1H,  $^3J_{HH} = 7.8$  Hz, 4'-H), 2.21 (m, 1H, 4-H), 1.61 (dd, 3H,  $^3J_{HH} = 7.6$  Hz,  $^3J_{HH} = 4.8$  Hz,  $1_{syn-H}$ ), 1.57 (s, 3H,  $C_5H_3-CH_3$ ), 1.33 (dd, 3H,  $^3J_{HH} = 11.8$  Hz,  $^2J_{HH} = 4.8$  Hz,  $1_{anti-H}$ ), 0.17, -0.26 (each s, each 3H,  $Si(CH_3)_2$ ).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 148.5 (dm,  $^1J_{CF} = 250$  Hz, *o*- $B(C_6F_5)_3$ ), 138.0 (dm,  $^1J_{CF} = 240$  Hz, *p*- $B(C_6F_5)_3$ ), 137.6 (dm,  $^1J_{CF} = 250$  Hz, *m*- $B(C_6F_5)_3$ ), 136.3 (ipso-C of  $MeC_5H_3$ ), 132.5 (C2), 123.5 ( $C_5H_4$ ), 121.3 ( $MeC_5H_3$ ), 120.5 (C3), 120.4 ( $C_5H_4$ ), 107.7 ( $MeC_5H_3$ ), 106.5 ( $C_5H_4$ ), 106.0 ( $MeC_5H_3$ ), 105.3 ( $C_5H_4$ ), 104.0 (ipso-C of  $MeC_5H_3Si$ ), 100.9 (ipso-C of  $C_5H_4Si$ ), 53.5 (C1), 27 (br, C4), 14.5 ( $C_5H_3-CH_3$ ), -6.4, -8.1 ( $Si(CH_3)_2$ ).

**E-18'b (Minor E Isomer):**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 6.01, 5.78 (each m, each 1H,  $C_5H_4$ ), 5.70 (m, 1H, 2-H), 5.64 (m, 1H,  $MeC_5H_3$ ), 5.51 (m, 1H,  $MeC_5H_3$ ), 5.46 (m, 1H,  $C_5H_4$ ), 5.38 (m, 1H, 3-H), 4.41 (m, 1H,  $C_5H_4$ ), 3.89 (br s, 1H,  $MeC_5H_3$ ), 2.51 (br d, 1H,  $^3J_{HH} = 12.6$  Hz, 4'-H), 2.18 (m, 1H, 4-H), 1.72 (s, 3H,  $C_5H_3-CH_3$ ), 1.67 (dd, 1H,  $^3J_{HH} = 12.6$  Hz,  $^2J_{HH} = 4.8$  Hz,  $1_{anti-H}$ ), 1.48 (dd, 1H,  $^3J_{HH} = 8.4$  Hz,  $^2J_{HH} = 4.8$  Hz,  $1_{syn-H}$ ), 0.22, -0.23 (each s, each 3H,  $Si(CH_3)_2$ ).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 148.5 (dm,  $^1J_{CF} = 250$  Hz, *o*- $B(C_6F_5)_3$ ), 138.0 (dm,  $^1J_{CF} = 240$  Hz, *p*- $B(C_6F_5)_3$ ), 137.6 (dm,  $^1J_{CF} = 250$  Hz, *m*- $B(C_6F_5)_3$ ), 136.5 (ipso-C of  $MeC_5H_3$ ), 129.1 (C2), 124.0 ( $C_5H_4$ ), 121.9 ( $C_5H_4$ ), 121.8 ( $MeC_5H_3$ ), 114.4 (C3), 110.2 ( $C_5H_4$ ), 109.1 ( $MeC_5H_3$ ), 108.1 ( $MeC_5H_3$ ), 105.8 ( $C_5H_4$ ), 105.6 (ipso-C of  $MeC_5H_3Si$ ), 101.9 (ipso-C of  $C_5H_4Si$ ), 51.4 (C1), 27 (br, C4), 13.3 ( $C_5H_3-CH_3$ ), -6.4, -7.5 ( $Si(CH_3)_2$ ).

**(18c):** Reaction of **17c** (20 mg, 48.3  $\mu$ mol) with tris(pentafluorophenyl)borane (24.7 mg, 48.3  $\mu$ mol) gave **18c**.

**Z-18c:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 268 K):  $\delta$  = 5.90 (pt, 1H,  $cyC_5H_3$ ), 5.37, 5.31 (each m, each 1H,  $C_5H_4$ ), 5.22 (m, 1H, 2-H), 5.06 (m, 1H, 3-H), 5.02 (pt, 1H,  $cyC_5H_3$ ), 4.95 (m, 2H,  $cyC_5H_3$ ,  $C_5H_4$ ), 4.41 (m, 1H,  $C_5H_4$ ), 3.24 (m, 1H, *CH* of cy), 2.66 (pt, 1H,  $1_{syn-H}$ ), 1.90-0.80 (10H, *CH* of cy), 0.44 (m, 1H,  $1_{anti-H}$ ), 0.33, -0.03 (each s, each 3H,  $Si(CH_3)_2$ ), -0.36 (br, 1H, 4'-H), -1.79 (br, 1H, 4-H).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 268 K):  $\delta$  = 145.3 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ), 141.2 (ipso-C of  $cyC_5H_3$ ), 137.2 (dm,  $^1J_{CF} = 250$  Hz, *p*- $B(C_6F_5)_3$ ), 136.8 (dm,  $^1J_{CF} = 240$  Hz, *m*- $B(C_6F_5)_3$ ), 127.2 (C2), 121.2 ( $C_5H_4$ ), 119.3 ( $cyC_5H_3$ ), 115.3 ( $C_5H_4$ ), 112.3 (C3), 110.8 ( $cyC_5H_3$ ), 109.0 ( $cyC_5H_3$ ), 105.5, 103.9 ( $C_5H_4$ ), 102.7 (ipso-C of  $cyC_5H_3Si$ ), 99.8 (ipso-C of  $C_5H_4Si$ ), 58.3 (*CH* of cy), 55.2 (C1), 33.1, 27.8, 27.6, 24.9, 23.6 (*CH* of cy), 25 (br, C4), -5.1, -6.3 ( $Si(CH_3)_2$ ).

**E-18c:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 268 K):  $\delta$  = 6.04 (m, 1H,  $C_5H_4$ ), 5.82 (m, 1H,  $cyC_5H_3$ ), 5.79 (m, 1H,  $C_5H_4$ ), 5.77 (m, 1H, 2-H), 5.48 (m, 1H, 3-H), 5.46 (m, 1H,  $C_5H_4$ ), 5.43 (m, 1H,  $cyC_5H_3$ ), 4.52 (m, 1H,  $cyC_5H_3$ ), 4.46 (m, 1H,  $C_5H_4$ ), 3.12 (m, 1H, *CH* of cy),

2.54 (br d, 1H,  $^2J_{HH} = 17.4$  Hz, 4'-H), 2.22 (dd, 1H,  $^2J_{HH} = 17.4$  Hz,  $^3J_{HH} = 7.2$  Hz, 4-H), 1.90-0.80 (10H, *CH* of cy), 1.67 (m, 1H,  $1_{syn-H}$ ), 1.59 (m, 1H,  $1_{anti-H}$ ), 0.21, -0.19 (each s, 3H,  $Si(CH_3)_2$ ).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 268 K):  $\delta$  = 148.5 (dm,  $^1J_{CF} = 250$  Hz, *o*- $B(C_6F_5)_3$ ), 139.3 (ipso-C of  $cyC_5H_3$ ), 137.9 (dm,  $^1J_{CF} = 240$  Hz, *p*- $B(C_6F_5)_3$ ), 137.2 (dm,  $^1J_{CF} = 240$  Hz, *m*- $B(C_6F_5)_3$ ), 131.3 (C2), 123.8, 121.3 ( $C_5H_4$ ), 120.4 (C3), 118.0 ( $cyC_5H_3$ ), 109.9 ( $C_5H_4$ ), 107.3, 105.5 ( $cyC_5H_3$ ), 102.8 ( $C_5H_4$ ), 102.1 (ipso-C of  $cyC_5H_3Si$ ), 100.4 (ipso-C of  $C_5H_4Si$ ), 58.4 (*CH* of cy), 51.0 (C1), 32.1, 25.8 (2 $\times$ ), 25.2, 23.6 (*CH* of cy), 27 (br, C4), -3.5, -4.3 ( $Si(CH_3)_2$ ).

**(18d):** Reaction of **17d** (20 mg, 53.5  $\mu$ mol) with tris(pentafluorophenyl)borane (27.3 mg, 53.5  $\mu$ mol) gave **18d**.

**Z-18d:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 298 K):  $\delta$  = 6.10 (m, 1H,  $C_5H_4$ ), 5.99 (m, 1H,  $^iPrC_5H_3$ ), 5.80 (m, 1H,  $C_5H_4$ ), 5.51 (m, 1H,  $^iPrC_5H_3$ ), 5.51 (m, 1H,  $C_5H_4$ ), 5.24 (m, 1H, 2-H), 4.55 (m, 1H, 3-H), 4.23 (m, 1H,  $^iPrC_5H_3$ ), 4.16 (m, 1H,  $C_5H_4$ ), 2.71 (t, 1H,  $^3J_{HH} = 9.0$  Hz,  $1_{syn-H}$ ), 2.21 (sept, 1H,  $^3J_{HH} = 6.8$  Hz,  $^iPr-CH$ ), 1.15 (m, 1H,  $1_{anti-H}$ ), 0.94, 0.73 (each d, each 3H,  $^3J_{HH} = 6.8$  Hz,  $^iPr-CH_3$ ), 0.31, -0.08 (each s, each 3H,  $Si(CH_3)_2$ ), -0.30 (br, 1H, 4'-H), -1.90 (br, 1H, 4-H).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 298 K):  $\delta$  = 149.4 (ipso-C of  $^iPrC_5H_3$ ), 145.1 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ), 138.8 (dm,  $^1J_{CF} = 250$  Hz, *p*- $B(C_6F_5)_3$ ), 137.6 (dm,  $^1J_{CF} = 240$  Hz, *m*- $B(C_6F_5)_3$ ), 128.5 (C2), 117.6 ( $C_5H_4$ ), 116.3 ( $^iPrC_5H_3$ ), 113.6 ( $C_5H_4$ ), 113.5 ( $^iPrC_5H_3$ ), 110.5 ( $C_5H_4$ ), 110.1 (C3), 105.7 (ipso-C of  $^iPrC_5H_3Si$ ), 105.4 ( $C_5H_4$ ), 104.2 ( $^iPrC_5H_3$ ), 103.9 (ipso-C of  $C_5H_4Si$ ), 55.2 (C1), 29.6 ( $^iPr-CH$ ), 25 (br, C4), 22.8, 22.1 ( $^iPr-CH_3$ ), -6.3, -6.5 ( $Si(CH_3)_2$ ).

**E-18d:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 298 K):  $\delta$  = 6.04 (m, 1H,  $C_5H_4$ ), 5.85 (m, 1H,  $^iPrC_5H_3$ ), 5.82 (m, 1H,  $C_5H_4$ ), 5.77 (m, 1H, 2-H), 5.48 (m, 1H,  $C_5H_4$ ), 5.48 (m, 1H, 3-H), 5.43 (m, 1H,  $^iPrC_5H_3$ ), 4.57 (pt, 1H,  $^iPrC_5H_3$ ), 4.54 (m, 1H,  $C_5H_4$ ), 2.49 (t, 1H,  $^2J_{HH} = 18.6$  Hz, 4'-H), 2.45 (sept, 1H,  $^3J_{HH} = 6.8$  Hz,  $^iPr-CH$ ), 2.22 (dd, 1H,  $^2J_{HH} = 18.6$  Hz,  $^3J_{HH} = 7.2$  Hz, 4-H), 1.70 (m, 1H,  $1_{syn-H}$ ), 1.60 (m, 1H,  $1_{anti-H}$ ), 1.12, 0.97 (each d, each 3H,  $^3J_{HH} = 6.8$  Hz,  $^iPr-CH_3$ ), 0.22, -0.21 (each s, each 3H,  $Si(CH_3)_2$ ).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 298 K):  $\delta$  = 149.0 (ipso-C of  $^iPrC_5H_3$ ), 148.5 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ), 137.8 (dm,  $^1J_{CF} = 250$  Hz, *p*- $B(C_6F_5)_3$ ), 137.4 (dm,  $^1J_{CF} = 240$  Hz, *m*- $B(C_6F_5)_3$ ), 127.1 (C2), 123.9, 122.9 ( $C_5H_4$ ), 118.1 ( $^iPrC_5H_3$ ), 110.5 ( $C_5H_4$ ), 110.5 (C3), 107.8 ( $^iPrC_5H_3$ ), 105.7 ( $C_5H_4$ ), 105.1 (ipso-C of  $^iPrC_5H_3Si$ ), 103.4 ( $^iPrC_5H_3$ ), 101.0 (ipso-C of  $C_5H_4Si$ ), 51.3 (C1), 29 (br, C4), 28.0 ( $^iPr-CH$ ), 24.2, 22.1 ( $^iPr-CH_3$ ), -5.4, -7.4 ( $Si(CH_3)_2$ ).

**(18e):** Reaction of **17e** (20 mg, 51.6  $\mu$ mol) with tris(pentafluorophenyl)borane (26.4 mg, 51.6  $\mu$ mol) gave **18e**.

**Z-18e:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 5.95 (m, 1H,  $^tBuC_5H_3$ ), 5.36 (m, 1H,  $C_5H_4$ ), 5.31 (m, 1H,  $C_5H_4$ ), 5.08 (m, 1H,  $^tBuC_5H_3$ ), 5.08 (m, 1H, 2-H), 4.95 (m, 1H,  $^tBuC_5H_3$ ), 4.86 (m, 1H,  $C_5H_4$ ), 4.54 (m, 1H, 3-H), 4.39 (m, 1H,  $C_5H_4$ ), 2.54 (t, 1H,  $^3J_{HH} = 9.6$  Hz,  $1_{syn-H}$ ), 0.95 (m, 1H,  $1_{anti-H}$ ), 0.83 (s, 9H,  $^tBu-CH_3$ ), 0.14, 0.13 (each s, each 3H,  $Si(CH_3)_2$ ), -0.39 (br d, 1H,  $^3J_{HH} = 10.8$  Hz, 4'-H), -1.74 (br, 1H, 4-H).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 156.3 (ipso-C of  $^tBuC_5H_3$ ), 145.1 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ), 137.4 (dm,  $^1J_{CF} = 250$  Hz, *p*- $B(C_6F_5)_3$ ), 136.8 (dm,  $^1J_{CF} = 240$  Hz, *m*- $B(C_6F_5)_3$ ), 133.9 (C2), 115.2, 114.5, 112.0 ( $C_5H_4$ ), 110.6 (C3), 110.0 (ipso-C of  $^tBuC_5H_3Si$ ), 109.1, 108.1 ( $^tBuC_5H_3$ ), 108.1 ( $C_5H_4$ ), 99.3 (ipso-C of  $C_5H_4Si$ ), 98.3 ( $^tBuC_5H_3$ ), 55.8 (C1), 34.1 ( $^tBu-CH_3$ ), 33.4 ( $C(CH_3)_3$ ), 24 (br, C4), -4.7, -7.8 ( $Si(CH_3)_2$ ).

**E-18e:**  $^1H$  NMR (599.9 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 6.06 (m, 1H,  $C_5H_4$ ), 5.78 (ddd, 1H,  $^3J_{HH} = 16.2$  Hz,  $^3J_{HH} = 14.8$  Hz,  $^3J_{HH} = 9.6$  Hz, 2-H), 5.73 (m, 1H,  $C_5H_4$ ), 5.73 (m, 1H,  $^tBuC_5H_3$ ), 5.62 (dd, 1H,  $^3J_{HH} = 16.2$  Hz,  $^3J_{HH} = 8.4$  Hz, 3-H), 5.45 (m, 1H,  $^tBuC_5H_3$ ), 5.38 (m, 1H,  $C_5H_4$ ), 4.46 (m, 1H,  $^tBuC_5H_3$ ), 4.36 (m, 1H,  $C_5H_4$ ), 2.66 (d, 1H,  $^2J_{HH} = 18.0$  Hz, 4'-H), 2.44 (dd, 1H,  $^2J_{HH} = 18.0$  Hz,  $^3J_{HH} = 8.4$  Hz, 4-H), 1.59 (d, 1H,  $^3J_{HH} = 9.6$  Hz,  $1_{syn-H}$ ), 1.49 (d, 1H,  $^3J_{HH} = 14.8$  Hz,  $1_{anti-H}$ ), 1.02 (s, 9H,  $^tBu-CH_3$ ), 0.16, -0.25 (each s, each 3H,  $Si(CH_3)_2$ ).  $^{13}C$   $\{^1H\}$  NMR (150.8 MHz,  $[D_8]$ toluene, 258 K):  $\delta$  = 153.2 (ipso-C of  $^tBuC_5H_3$ ), 148.4 (dm,  $^1J_{CF} = 240$  Hz, *o*- $B(C_6F_5)_3$ ),

137.6 (dm,  $^1J_{CF} = 250$  Hz, *p*-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 137.2 (dm,  $^1J_{CF} = 240$  Hz, *m*-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 132.2 (C2), 124.2 (C3), 124.2 (BuC<sub>5</sub>H<sub>3</sub>), 122.6, 119.2, 109.7 (C<sub>5</sub>H<sub>4</sub>), 107.8 (BuC<sub>5</sub>H<sub>3</sub>), 104.9 (C<sub>5</sub>H<sub>4</sub>), 103.2 (ipso-C of BuC<sub>5</sub>H<sub>3</sub>-Si), 100.9 (BuC<sub>5</sub>H<sub>3</sub>), 99.6 (ipso-C of C<sub>5</sub>H<sub>4</sub>Si), 51.1 (C1), 30.5 (Bu-CH<sub>3</sub>), 27 (br, C4), 29.9 (C(CH<sub>3</sub>)<sub>3</sub>), -5.9, -7.4 (Si(CH<sub>3</sub>)<sub>2</sub>).

**Methyl Methacrylate Polymerization (PMMA).** The polymerization reactions were carried out in the dark at 0 °C in dichloromethane (5 mL), which was dried with P<sub>2</sub>O<sub>5</sub> or CaH<sub>2</sub> and freshly condensed prior to use. Also, directly before use, the MMA monomer was dried by stirring it with calcium hydride for 2 h. Subsequently the MMA was condensed in a flask, and 0.2 mL of triethylaluminum was added. After agitation for 30 min the monomer (2 mL) was condensed directly into the reaction flask. Injecting a solution of the respective freshly prepared zirconocene/borane system in dichloromethane (1 mL) started the polymerization reaction. After 1 h the reaction was quenched by adding methanol (2 mL). Then all volatiles were removed in vacuo; the obtained PMMA was dried and characterized by NMR. The {[isopropylidene(cyclopentadienyl)(1-indenyl)]methylzirconium} {methyltris(pentafluorophenyl)borate} system was used as a catalyst standard for the MMA polymerization reactions. Molecular weights and polydispersities of the PMMA polymers were obtained by GPC (Agilent GPC equipped with a switchable UV detector (254 nm) and a refractive index detector operating with a flow rate of 1 mL of THF (HPLC grade) per minute) with two PSSVB columns (100 000 and 1000 Å; MZ

Analysetechnik) at 35 °C. The polymer samples (20 mg) were dissolved in THF (HPLC grade, 2–3 mL), and the solution was filtered before the injection. The measured data were analyzed with WinGPC6 relative to polystyrene standards. The stereochemical triad analyses were carried out by <sup>1</sup>H NMR (599.9 MHz) experiments at 25 °C, using PMMA (50–60 mg) in CDCl<sub>3</sub> solutions.<sup>57</sup>

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**Supporting Information Available:** Details of the X-ray crystal structure analyses. Details of the syntheses of the *ansa*-metallocene precursors. Additional spectroscopic features of the metallocene systems. ES-MS of the anions formed by reaction of MMA with the catalyst system **16**. Additional data of the polymerization experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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