

## Alkoxy- and Aryloxyboratabenzene Complexes of Zirconium

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**Abstract:** Addition of primary and secondary alcohols to  $C_5H_5B-PMe_3$  (**2**) affords 1-alkoxyboracyclohexa-2,4-dienes in high yields. Deprotonation of these boracyclohexadienes, using NaH or lithium diisopropylamide, followed by the reaction with  $ZrCl_4$  allows for the coordination of alkoxyboratabenzene ligands to zirconium. Thus, complexes of the type  $[C_5H_5B-OR]_2ZrCl_2$  ( $R = Et$ , **1**;  $Cy$ , **3**;  $Ph$ , **4**; and  $CH_2Ph$ , **5**) can be produced in 45–65% overall yield. The crystallographically determined molecular structure of **4** shows evidence for B–O  $\pi$  orbital overlap. The linked diols 1,2-*trans*-cyclohexanediol and binaphthol can be used to generate ansa-type zirconium complexes **7** and **9**, respectively. When **1**, **3**, **4**, or **5** react with  $(AlMe_3)_2$  the organometallic product is  $[C_5H_5B-Me]_2ZrCl_2$  (**10**).  $Cp^*[C_5H_5B-OEt]ZrCl_2$  (**11**,  $Cp^* = C_5Me_5$ ) and  $(AlMe_3)_2$  give  $Cp^*[C_5H_5B-Me]ZrCl_2$  (**13**). The complex  $Cp^*[C_5H_5B(OEt)(AlMe_3)]ZrCl_2$  (**12**) appears to be an intermediate in the conversion of **11** to **13**. A comparison of the molecular structures of **11** and **12** shows that the B–O interaction weakens and the Zr–B distance contracts upon adduct formation. Complexes **1**, **3**, **4**, **9**, **10**, and  $[C_5H_5B-Ph]_2ZrCl_2$  (**14**) react with excess methylaluminoxane (MAO) and ethylene (1 atm) to give a Flory–Shultz distribution of olefins. For **7**/MAO, ethylene addition results in the formation of polyethylene. The overall activity toward monomer and selectivity for linear 1-alkenes of the catalyst solutions are determined by the exocyclic group of the alkoxyboratabenzene zirconium precursor.

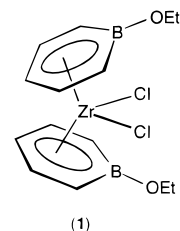
## Introduction

The oligomerization of ethylene to linear 1-alkenes ( $\alpha$ -olefins) is a metal-mediated process of major industrial importance.<sup>1</sup> Close to 4 billion pounds are used in a variety of applications including the synthesis of detergents, plasticizers, lubricants, and linear alcohols. More recently, they are finding use as comonomers in the preparation of linear low-density polyethylene (LLDPE).<sup>2</sup> Current  $\alpha$ -olefin production requires elevated temperatures and pressures. The neutral nickel-based catalysts used in the shell higher olefin process (SHOP) operate at 80–120 °C and 1000–2000 psi and take advantage of a multiphase reaction medium to separate the products and maximize selectivity.<sup>1c</sup> Triethylaluminum may also be used, either catalytically or stoichiometrically at 120 °C and approximately 2000 psi.<sup>1b</sup>

Current efforts are focused on lowering the monomer pressure of the oligomerization reaction by the use of cationic, well-defined organometallic catalysts. Keim and Tkatchenko reported that nickel catalysts activated by methylaluminoxane (MAO) give much higher turnover frequencies than their neutral counterparts.<sup>3</sup> Brookhart also developed cationic Ni(II) diimine catalysts that oligomerize ethylene to straight chain olefins by

tailoring the ligand framework.<sup>4</sup> More recently, a similar strategy was extended to pyridinebis(imine) complexes of iron and cobalt which, after treatment with MAO, display remarkable ethylene consumption activity.<sup>5</sup> Reduced monomer pressure may open opportunities for more energy efficient process conditions and less costly reactor designs.

We recently reported that  $[C_5H_5B-OEt]_2ZrCl_2$  (**1**) with excess MAO oligomerizes ethylene at 1 atm to a distribution of 1-alkenes.<sup>6</sup> Ethylene consumption by **1**/MAO occurs at rates that are competitive with those displayed by polymerization catalysts derived from metallocene precursors.<sup>7</sup> The preference for 1-alkene production by **1**/MAO is a result of increased rates of  $\beta$ -hydrogen elimination, relative to standard metallocenes, together with a reluctance to react with 1-alkenes. This selectivity increases the scope of reactions mediated by group 4 single site catalysts and demonstrates the utility of boratabenzene ligands<sup>8</sup> in designing novel catalysts.<sup>9</sup>



Despite their potential, little is known of the reactivity of the alkoxyboratabenzene ligand within electrophilic, early transition

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metal complexes. In particular, the relationship between the steric size of the exocyclic alkoxy group and the selectivity of the oligomerization reaction is unclear. Furthermore, the effect of restricting rotation of the boratabenzene ligands by use of a connecting bridge has not been studied.

In this contribution we explore the scope of ethylene oligomerization catalysts derived from bis(alkoxyboratabenzene)zirconium dichloride complexes. An improved method for the synthesis of alkoxy-substituted boratabenzene ligands which can be used to append a variety of alkoxy substituents under mild conditions is reported. Modification of the substituent on boron provides a handle to modify the selectivity of the active species. Finally, we present studies on the reactivity of trimethylaluminum with zirconium-bound alkoxyboratabenzene ligands because this interaction is important in determining the selectivity of MAO-activated catalysts.

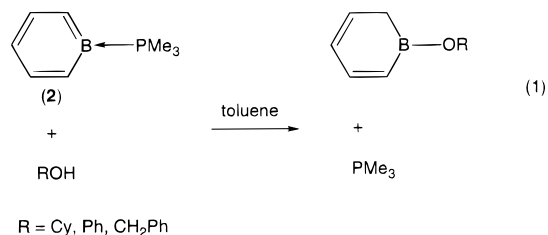
## Results and Discussion

**Ligand Synthesis.** Several approaches exist in the literature for accessing alkoxy-boratabenzene anions. Ashe reported that 1-bromoboracyclohexa-2,5-diene and dimethyl ether produce 1-methoxyboracyclohexa-2,5-diene, which may be subsequently deprotonated or used directly in the synthesis of  $[\text{C}_5\text{H}_5\text{B}-\text{OMe}]_2\text{Fe}$ .<sup>10</sup> Herberich showed that, under metalation conditions, 2,4-pentadienylboranes give borabenzene derivatives via a spontaneous ring closure. Subsequent tautomerization provides alkoxy-substituted boratabenzene salts.<sup>11</sup> More recently, Fu demonstrated that nucleophilic attack of NaOEt on the trimethylphosphine adduct of borabenzene (**2**) results in the formation of  $\text{Na}[\text{C}_5\text{H}_5\text{B}-\text{OEt}]$ .<sup>12</sup>

Our interest in investigating the effect of alkoxy substitution on the selectivity of catalysts derived from complexes such as **1** led us to consider an alternative synthesis of alkoxyboratabenzene salts. The approach by Fu is direct but sensitive to the steric bulk and the basicity of the incoming nucleophile. We found that for some alkoxides the desired reactions did not occur or were slow. For example, the reaction of sodium 4-*tert*-butylphenoxide with **2** in tetrahydrofuran (THF) is slow and results in the formation of a mixture of products (by <sup>1</sup>H NMR spectroscopy). There is no reaction in the case of disodium binaphtholate, probably as a result of the low solubility of the disodium salt.

In the process of these efforts we discovered that the addition of alcohols to **2** provides 1-alkoxyboracyclohexa-2,4-diene, as shown in eq 1.

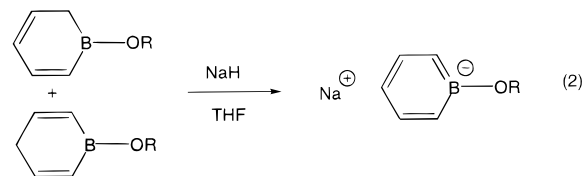
The reactions shown in eq 1 occur at convenient rates. For example, addition of 1 equiv of benzyl alcohol to **2** results in 1-benzyloxyboracyclohexa-2,4-diene within 15 min at a concentration of approximately 0.15 M, as determined by <sup>1</sup>H NMR spectroscopy. Most diagnostic is the appearance of a singlet at



4.70 ppm (B—OCH<sub>2</sub>Ph) which grows at the expense of the doublet at 4.33 ppm (HOCH<sub>2</sub>Ph). In addition, the doublet at 0.79 ppm, which is due to free  $\text{PMe}_3$ , intensifies as the reaction progresses. A broad doublet centered at 1.68 ppm, which is due to the methylene hydrogens in the ring, is also consistent with the presence of a boracyclohexa-2,4-diene species. Reactions with *tert*-butyl alcohol and **2** fail, probably as a result of the increased steric bulk on the oxygen atom.

For all compounds studied thus far, the original boracyclohexa-2,4-diene isomerizes to the 2,5-diene, ultimately reaching an approximately 1:1 mixture. Similar thermodynamic ratios have been observed for other amino- and alkoxy-substituted boracyclohexadienes.<sup>11,13</sup> <sup>11</sup>B NMR data provide supporting information for these reactions. The disappearance of a sharp doublet at 21 ppm and formation of a broad singlet at 48 ppm are consistent with the loss of **2** and formation of an alkoxy- or aryloxyboracyclohexa-2,4-diene.<sup>11</sup> Isomerization to the 2,5-diene isomer is also supported by the subsequent appearance of a broad signal at 39 ppm.

In practice, the boracyclohexadienes are not isolated but are deprotonated immediately using a slurry of NaH in THF, leading to the sodium salt of the corresponding alkoxyboratabenzene in excellent yields (eq 2). The success of the deprotonation reaction hinges on the complete removal of the trimethylphosphine byproduct in eq 1. Isolation of  $\text{Na}[\text{C}_5\text{H}_5\text{B}-\text{OR}]$  is carried out by filtration of excess NaH and subsequent removal of THF. For  $\text{Na}[\text{C}_5\text{H}_5\text{B}-\text{OPh}]$ , purification was done by trituration in Et<sub>2</sub>O/pentane. Lithium diisopropylamide (LDA) in THF at -78 °C may also be used for deprotonation and generation of the more soluble lithium salts. In all cases, the <sup>11</sup>B NMR boratabenzene signals in THF-*d*<sup>8</sup> occur in the 39–41 ppm range.



## Zirconium Complexes Containing Alkoxyboratabenzene

**Ligands.** The coordination of alkoxyboratabenzene ligands to zirconium is straightforward and takes advantage of previously established protocols.<sup>14</sup> As shown in eq 3, the direct reaction of  $\text{ZrCl}_4$  with two equiv of  $\text{Na}[\text{C}_5\text{H}_5\text{B}-\text{OR}]$  in Et<sub>2</sub>O at -78 °C affords the bis(boratabenzene)zirconium dichloride species in good yield. For  $\text{Na}[\text{C}_5\text{H}_5\text{B}-\text{OPh}]$ , the reaction works better in heptane. The bis(alkoxy- or aryloxyboratabenzene)zirconium dichloride products range in color from golden yellow to orange-yellow and they are isolated as crystalline solids with similar solubility properties. They are insoluble in pentane, slightly soluble in Et<sub>2</sub>O, and considerably more soluble in aromatic

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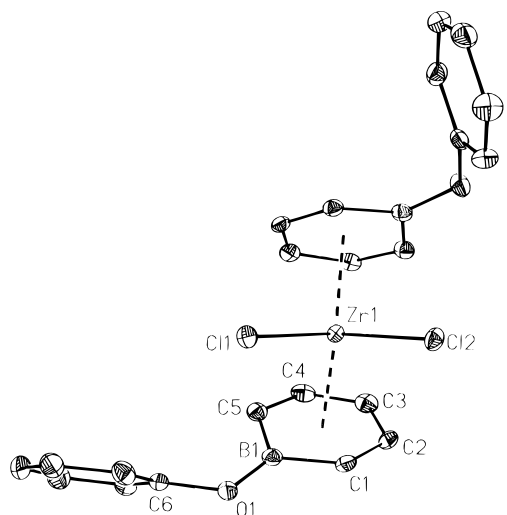
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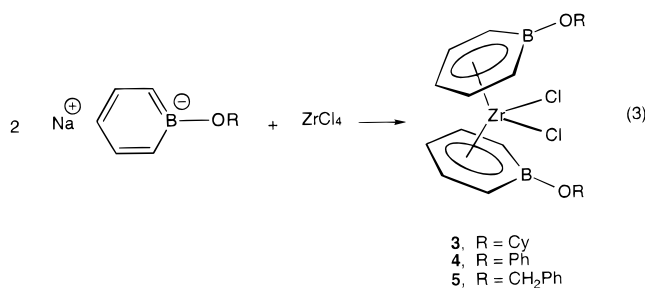
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**Figure 1.** ORTEP view of **4**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–Cl(1), 2.431(1); Zr(1)–Cl(2), 2.423(1); Zr(1)–C(1), 2.666(3); Zr(1)–C(2), 2.587(3); Zr(1)–C(3), 2.503(3); Zr(1)–C(4), 2.571(3); Zr(1)–C(5), 2.628(3); Zr(1)–B(1), 2.854(3); B(1)–O(1), 1.385(4); O(1)–C(6), 1.383(3). Selected bond angles: centroid–Zr–centroid, 136.4(2)°; B(1)–O(1)–C(6), 125.4(2)°.

solvents, THF, or  $\text{CH}_2\text{Cl}_2$ . Trituration with pentane or mixtures of ether and pentane removes impurities.



Single crystals suitable for X-ray diffraction were obtained for  $[\text{C}_5\text{H}_5\text{B}(\text{OPh})_2\text{ZrCl}_2]$  (**4**) and the results of this study are shown in Figure 1. The structure adopts a geometry similar to a bent metallocene and does not deviate significantly from that of **1**.<sup>6</sup> Whereas **1** contains a crystallographically imposed  $C_2$  axis, and therefore, equivalent boratabenzene fragments, the structure of **4** exhibits two inequivalent boratabenzene ligands. Both ligands, however, bind to Zr in a nearly identical fashion. The  $\text{sp}^2$  hybridization at oxygen and the average Zr–B distance of 2.854(3) Å indicate that the Zr–B orbital overlap is similar in **4** and **1** ( $d(\text{Zr}–\text{B}) = 2.83(1)$  Å). The centroid–Zr–centroid angle in **4** ( $136.4^\circ$ ) is also nearly identical to that of **1** ( $136.2^\circ$ ), and the average B–O distance (1.390(4) Å) in **4** is somewhat longer than that of **1** (1.372(4) Å). For comparison, the B–O bond lengths in  $\text{Li}[\text{B}(\text{OMe})_4]$  are in the range of 1.451(3)–1.475(4) Å.<sup>15</sup> In  $d^8$ -toluene the  $^1\text{H}$  NMR spectra of **4** shows non-diastereotopic boratabenzene rings, even at temperatures as low as 190 K. Therefore, it appears that the B–O  $\pi$ -bond is not strong.<sup>16</sup>

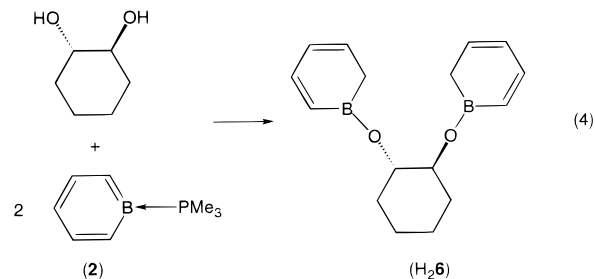
**Linked Structures.** *Ansa*-metallocenes refer to complexes which contain two cyclopentadienyl cores linked by an inter-

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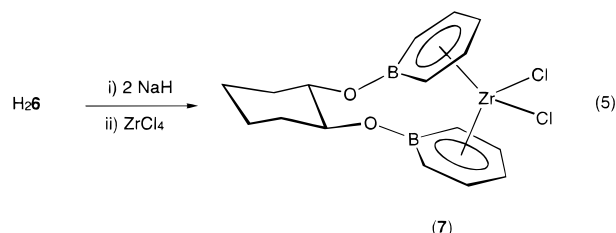
(16) The rotational barrier of the B–N bond in  $[\text{C}_5\text{H}_5\text{B}(\text{N}(i\text{-Pr})_2)_2\text{ZrCl}_2]$  at  $62^\circ\text{C}$  is  $18.2 \pm 0.5$  kcal/mol.<sup>14</sup> See also ref 13 for discussions of B–N bond rotational barriers in aminoboratabenzene ligands.

annular bridge.<sup>17</sup> This link restricts free rotation of the rings thereby creating a more rigid stereochemical environment around the metal.<sup>18</sup> This strategy allows for the design of highly stereospecific polymerization catalysts<sup>19</sup> which is one of the fastest growing areas in metallocene chemistry.<sup>20,21</sup> *Ansa*-metallocenes are also more stable under catalytic conditions and produce higher molecular weight polymers than their unlinked counterparts.<sup>22,23</sup>

The reactivity shown in eq 1 allows synthesis of linked bis-boratabenzene ligands by use of a suitable diol and two equiv of **2**. Equation 4 shows the use of racemic 1,2-*trans*-cyclohexanediol to prepare **H<sub>2</sub>6**.  $^1\text{H}$  NMR spectroscopy shows that the reaction proceeds in high yield and confirms subsequent conversion to a mixture of 2,4- and 2,5-diene isomers.



Treatment of **H<sub>2</sub>6** with NaH in THF yields the corresponding bis-boratabenzene dianion with a coordinated molecule of THF,  $\text{Na}_2\text{6}(\text{THF})$ , in 84% yield. Subsequent addition of  $\text{ZrCl}_4$  affords complex **7**, as shown in eq 5. Whereas the  $^1\text{H}$  NMR spectrum of  $\text{Na}_2\text{6}(\text{THF})$  exhibits equivalent ortho and meta protons, the spectrum of **7** exhibits five inequivalent boratabenzene signals ( $\delta$  5.20, 5.96, 6.39, 7.04, and 7.71), consistent with a chiral framework around zirconium. Only one of two enantiomers is drawn in eq 5.



Crystals of **7** suitable for X-ray crystallography were grown from an  $\text{Et}_2\text{O}$ /pentane solution, and the result of this study is illustrated in Figure 2. The structure of **7** displays chiral  $C_2$  symmetry and a typical B–O interaction (average  $d(\text{B}–\text{O}) = 1.382(9)$  Å,  $\angle\text{B}–\text{O}–\text{C} = 124.0(6)^\circ$ ). The Zr–B distance (2.838(8) Å) is similar to that in **1** and **4**, suggesting that

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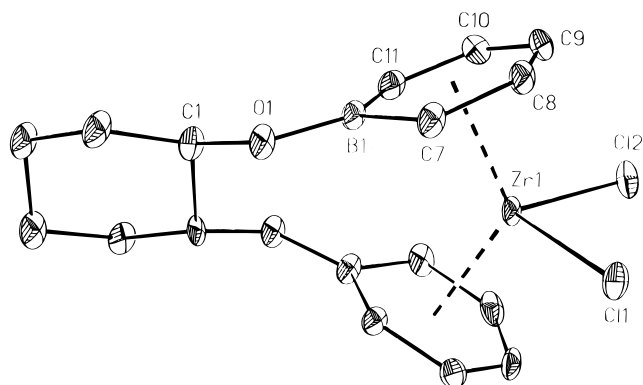
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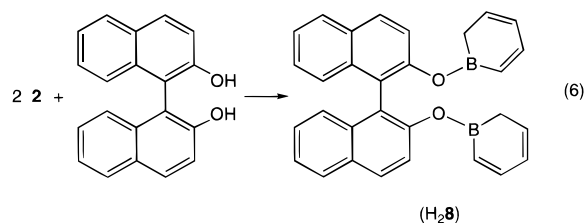




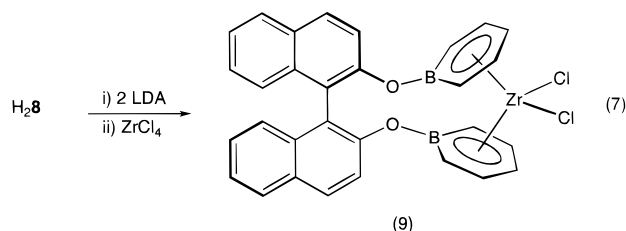
**Figure 2.** ORTEP view of **7**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–Cl(1), 2.440(2); Zr(1)–Cl(2), 2.424(2); Zr(1)–C(7), 2.619(7); Zr(1)–C(8), 2.574(7); Zr(1)–C(9), 2.528(7); Zr(1)–C(10), 2.568(7); Zr(1)–C(11), 2.655(7); Zr(1)–B(1), 2.838(8); B(1)–O(1), 1.387(9); O(1)–C(1), 1.441(8). Selected bond angles: Centroid–Zr–centroid, 124.6(7)°; B(1)–O(1)–C(1), 124.8(6)°.

boratabenzene ligands with exocyclic oxygen atoms have similar structural and binding properties. Closer inspection shows that the centroid–Zr–centroid angle in **7** is 125°, approximately 12° more acute than those in **1** or **4**. Therefore, the zirconium atom in **7** experiences a more open environment.

The sequence to the ansa structures also works well starting with binaphthol. Reaction of two equiv **2** with binaphthol gives **H<sub>2</sub>8** in eq 6, which is sufficiently pure to be used without further purification.

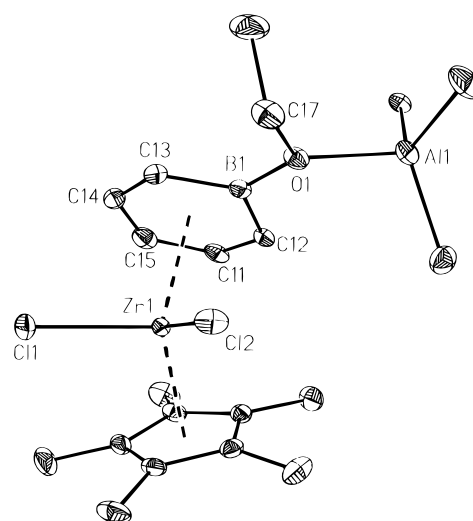


Deprotonation of **H<sub>2</sub>8** works well using LDA in THF at –78 °C. Double trituration in Et<sub>2</sub>O gives Li<sub>2</sub>8(THF)<sub>4</sub> as a white crystalline product. Reaction of Li<sub>2</sub>8(THF)<sub>4</sub> with ZrCl<sub>4</sub> in Et<sub>2</sub>O yields the corresponding zirconium complex **9**, as shown in eq 7. The tendency of **9** to precipitate as microcrystals frustrated efforts to obtain single crystals suitable for X-ray crystallography.



**Reactions with Trimethylaluminum.** Commercially available MAO contains a significant amount of trimethylaluminum, up to 35 wt % of overall aluminum. Trimethylaluminum is a result of incomplete hydrolysis and improves the solubility of MAO.<sup>24</sup> Because a large excess of MAO is added (on the basis of the ratio of Al to Zr) and because literature precedent exists for transmetalation reactions between the boron atom in

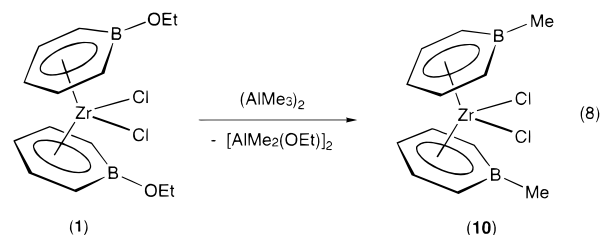
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**Figure 3.** ORTEP view of **12**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–Cl(1), 2.423(1); Zr(1)–Cl(2), 2.414(1); Zr(1)–C(11), 2.568(2); Zr(1)–C(12), 2.640(2); Zr(1)–C(13), 2.750(2); Zr(1)–C(14), 2.623(2); Zr(1)–C(15), 2.518(3); Zr(1)–B(1), 2.857(3); B(1)–O(1), 1.417(3); O(1)–C(17), 1.469(3); O(1)–Al(1), 1.964(2). Selected bond angles: B(1)–O(1)–C(17), 117.8(2)°; B(1)–O(1)–Al(1), 123.2(2)°; Al(1)–O(1)–C(17), 118.2(2)°.

boratabenzene ligands and aluminum,<sup>11</sup> we decided to investigate the reactions of **1** with trimethylaluminum.

When the reaction of **1** with one equiv of (AlMe<sub>3</sub>)<sub>2</sub> is monitored by <sup>1</sup>H NMR spectroscopy several new organometallic species are observed. After approximately 24 h, the reaction is complete and only one organometallic product remains together with [Me<sub>2</sub>(EtO)Al]<sub>2</sub>.<sup>25</sup> The organometallic product is [C<sub>5</sub>H<sub>5</sub>B–Me]<sub>2</sub>ZrCl<sub>2</sub> (**10**), which has been reported previously by Herberich.<sup>26</sup> Alkylation therefore occurs preferentially at boron instead of zirconium (eq 8).

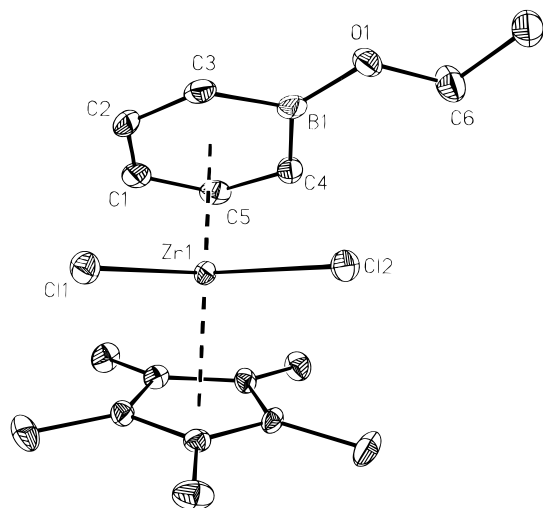


The <sup>1</sup>H NMR spectra in C<sub>6</sub>D<sub>6</sub> are greatly simplified when (AlMe<sub>3</sub>)<sub>2</sub> is reacted with Cp\* [C<sub>5</sub>H<sub>5</sub>B–OEt]ZrCl<sub>2</sub> (**11**). Only one intermediate species is observed, which exhibits diastereotopic boratabenzene ring resonances together with signals from a Cp\* ligand and coordinated AlMe<sub>3</sub> (–0.43 ppm, compare against (AlMe<sub>3</sub>)<sub>2</sub> at –0.33 ppm). The <sup>11</sup>B NMR of this intermediate (compound **12**) shows a peak at 38 ppm which argues against the formation of a bridging tetrahedral boron. The product at the end of the reaction is Cp\* [C<sub>5</sub>H<sub>5</sub>B–Me]ZrCl<sub>2</sub> (**13**).<sup>26</sup>

Single crystals of **12** suitable for an X-ray diffraction study were obtained by cooling the reaction immediately after trimethylaluminum addition. As shown in Figure 3, the exocyclic oxygen atom coordinates to aluminum forming a Lewis acid–

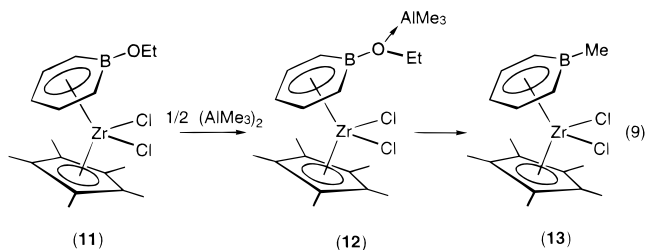
(25) Analysis confirmed by an independent synthesis from (AlMe<sub>3</sub>)<sub>2</sub> and EtOH.

(26) Spectroscopic data are identical to those reported for [C<sub>5</sub>H<sub>5</sub>B–Me]<sub>2</sub>ZrCl<sub>2</sub> in: Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751.

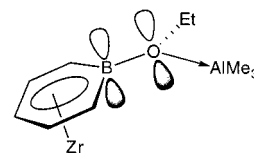


**Figure 4.** ORTEP view of **11**, showing the atom-numbering scheme. One of two independent molecules is illustrated. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–Cl(1), 2.444(1); Zr(1)–Cl(2), 2.448(1); Zr(1)–C(1), 2.492(4); Zr(1)–C(2), 2.618(4); Zr(1)–C(3), 2.729(4); Zr(1)–C(4), 2.626(4); Zr(1)–C(5), 2.550(4); Zr(1)–B(1), 2.882(5); B(1)–O(1), 1.382(6); O(1)–C(6), 1.425(5). Selected bond angle: B(1)–O(1)–C(6), 119.6(3)°.

base pair. The oxygen atom is  $sp^2$  hybridized ( $B-O-C = 117.8(2)^\circ$ ). The geometry about this atom is virtually planar, with the sum of the angles equaling  $359.2(6)^\circ$ . On this evidence we propose that alkylation at boron is preceded by coordination of  $AlMe_3$  and that the intermediate is compound **12** as shown in eq 9.



A crystallographic study of **11** was undertaken to probe any changes in Zr–boratabenzene binding upon coordination to  $AlMe_3$ . Figure 4 shows an ORTEP drawing of **11** and lists important metrical parameters (because two inequivalent molecules are present in the crystal, average values are reported). A comparison between the structures of **11** and **12** shows that there is a slight contraction of the Zr–B distance (2.882(5) Å for **11**, and 2.857(3) Å for **12**) upon adduct formation. The boratabenzene ring is rotated in both complexes such that the oxygen atom is nearly above one chloride ligand for both complexes. More significant is the B–O bond extension (1.382(6) Å average for **11**, and 1.417(3) Å for **12**) which indicates a less effective B–O  $\pi$  interaction in **12**. The average distance between Zr and the boratabenzene carbons does not change appreciably ( $d(Zr-C_{ave}) = 2.603(4)$  Å in **11** vs  $d(Zr-C_{ave}) = 2.619(2)$  Å in **12**). Taken together these data do not indicate a significant change in bonding. However, changes in the ligand periphery make an impact in the reactivity of the resulting catalysts (vide infra). Adduct formation with  $AlMe_3$  likely leads to a net removal of electron density from the boratabenzene ligand ultimately making zirconium in **12** more electrophilic than in **11**.



**Activation with MAO and Reactivity with Ethylene.** As mentioned in the Introduction, the ability of **1**/MAO to produce 1-alkenes under mild conditions indicates that metallocene-type complexes may find uses as homogeneous catalysts in the production of petrochemicals other than polyolefins.<sup>27</sup> Table 1 lists the selectivity and activity observed for complexes under similar reaction conditions (60 °C, 1000 [Al]/[Zr], [Zr] =  $1.2 \times 10^{-4}$  M, 30 min). In these experiments the activity was related to the total amount of ethylene uptake by weighing the reaction flask before and after the reaction. This procedure circumvents difficulties encountered in separating low molecular weight olefins from toluene. After aqueous quenching, the organic products were separated and the percentage distribution of 1-alkenes, 2-alkyl-1-alkenes, and 2-alkenes was determined by  $^1H$  NMR spectroscopy.

A comparison of entries 1–4 in Table 1 highlights the effect of oxygen substituents on the selectivity for 1-alkenes and on the overall ethylene consumption. Although the **1**/MAO combination remains the most selective, the highest activity corresponds to **4**/MAO. It is important to recall that in all cases 1-alkenes are the most likely initial product and that the formation of 2-alkyl-1-alkenes and 2-alkenes is the result of subsequent reactions. In our experimental setup the 1-alkenes and the catalyst are in the same phase.<sup>28</sup>

Entries 5 and 6 of Table 1 contain the data for the linked precatalysts **7** and **9**. **7**/MAO is the only case for which polymer precipitation is observed under one atm of ethylene. Differential scanning calorimetry (DSC) analysis shows a melting temperature of 118 °C for this product. The material shows no signs of branching by  $^{13}C$  NMR spectroscopy and these data are consistent with the formation of low molecular weight polyethylene. The binaphthol-containing **9** behaves similarly to the unlinked bis(alkoxyboratabenzene)zirconium precatalysts. Table 1 also contains entries for **10**/MAO and **14**/MAO (**14** =  $[C_5H_5B-Ph]_2ZrCl_2$ ).<sup>9b</sup> These data will be valuable when we consider the possibility of exchange reactions between boron and aluminum.

The olefins produced are described by a Schultz–Flory distribution of chain lengths.<sup>29</sup> This type of distribution can be characterized by a  $K$  factor, defined as:

$$K = \frac{[C_{n+2}]}{[C_n]} = \frac{1}{(1 + \beta)}$$

where  $\beta$  is the ratio of the rate of chain transfer (most likely

(27) For recent reviews on the use of metallocene complexes in the development of organic reactions, see: (a) Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12. (b) Buchwald, S. L.; Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12.

(28) The SHOP process circumvents this problem by allowing the 1-alkenes to diffuse into a phase in which the concentration of catalyst is much reduced. For aluminum reactions, a high concentration of ethylene discourages insertion of 1-alkenes into Al–H or Al–C bonds. For a detailed description of the SHOP process, see ref 1c and (a) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (b) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21.

(29) (a) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1935**, *30*, 379. (b) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *43*, 25. (c) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.

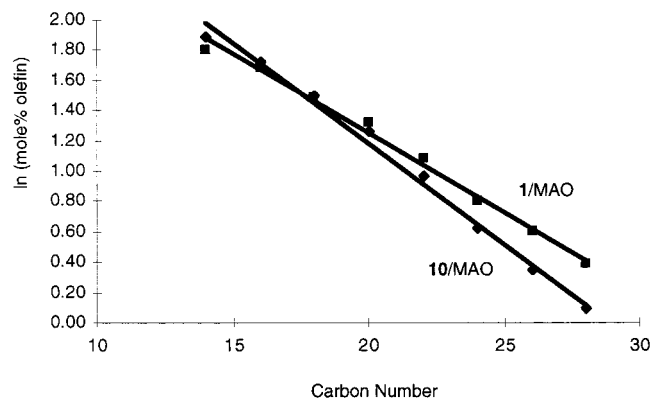
**Table 1.** Oligomerization Data for Bis-Boratabenzene Zirconium Complexes

precatalyst	% 1-alkenes <sup>c</sup>	% 2-alkyl-1-alkenes	% 2-alkenes	activity <sup>a</sup>
<b>1</b> <sup>b</sup>	95	5	trace	325
<b>3</b>	64	28	8	610
<b>4</b>	46	36	18	950
<b>5</b>	55	31	14	865
<b>7</b>	—	polymer	—	404
<b>9</b>	73	20	7	720
<b>10</b>	54	28	18	895
<b>14</b>	46	41	13	920

<sup>a</sup> Activity reported in kg [C<sub>2</sub>H<sub>4</sub>]/[Zr]·h. <sup>b</sup> See ref 6. <sup>c</sup> The error is estimated at ±2% from integration uncertainty in the <sup>1</sup>H NMR spectra.

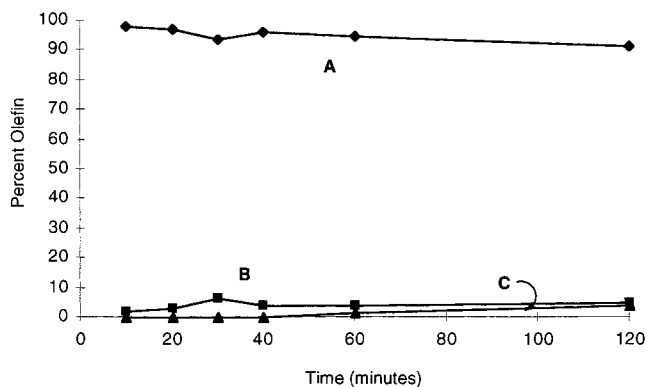
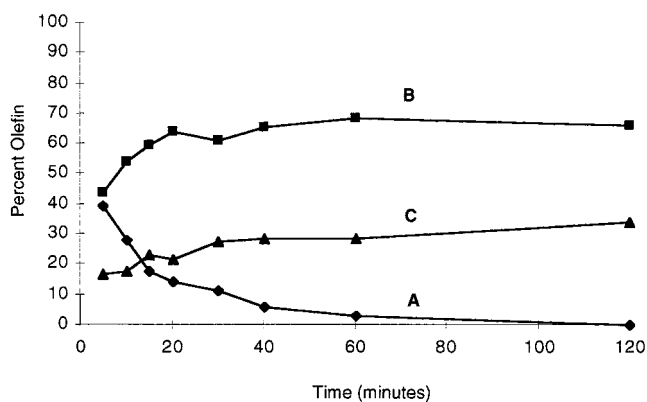
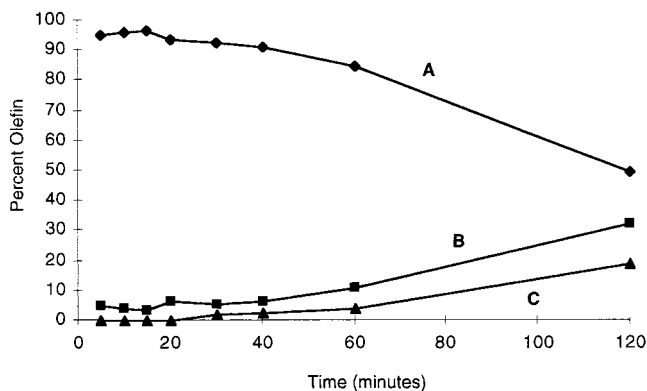
**Table 2.** K Factor Determination for Different Precatalysts

precatalyst	K factor
<b>1</b>	0.82
<b>3</b>	0.80
<b>4</b>	0.80
<b>5</b>	0.81
<b>9</b>	0.79
<b>10</b>	0.77

**Figure 5.** K factor determination. Plot of ln(mole % olefin) versus carbon number for C<sub>14</sub> through C<sub>28</sub> fractions for **1**/MAO and **10**/MAO.

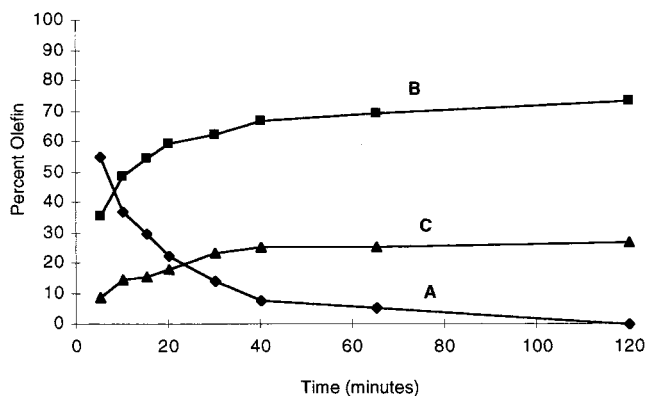
$\beta$ -hydride elimination for high valent zirconium) to the rate of propagation (ethylene insertion). K factor values for different catalysts under our standard conditions were determined by GC analysis of the C<sub>14</sub> through C<sub>28</sub> fraction and these data are listed in Table 2. A plot of ln(mole % olefin) versus carbon number for the **1**/MAO and **10**/MAO systems suggests that these solutions do not lead to the same catalyst (Figure 5).

The selectivity data in Table 1 do not necessarily reflect a reluctance of catalysts to react with 1-alkenes. For example, the high 1-alkene content for **1**/MAO may be a result of its lower activity relative to **3**/MAO. In the latter case the higher percentage of 2-alkyl-1-alkenes and 2-alkenes may arise from the higher concentration of 1-alkenes generated at shorter reaction times. To resolve these uncertainties, a series of catalysts prepared using MAO were reacted with 1-decene under identical reaction conditions ([Zr] = 5.6 × 10<sup>-4</sup> M; [Al]/[Zr] = 500; [1-decene] = 1.0 M in toluene; 25 °C). This concentration of 1-decene is approximately an order of magnitude higher than the final 1-alkene concentration generated during the ethylene oligomerization reactions described above. Aliquots of 0.8 mL were retrieved from the reaction mixture at regular intervals and quenched immediately with water. After separation, the olefin composition was determined in terms of terminal olefins (1-decene), internal olefins (2-decene), and dimers (2-

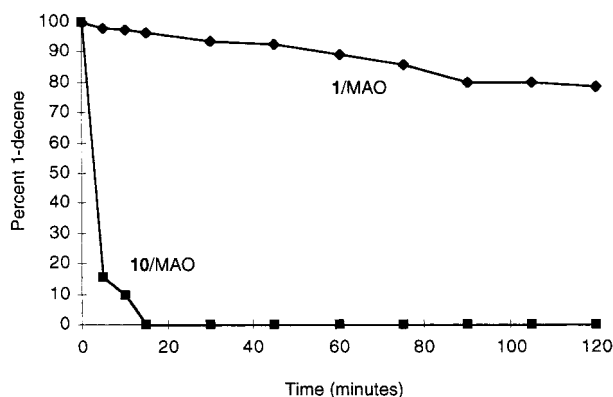
**Figure 6.** Reaction of **1**/MAO with 1-decene at 500 Al/Zr. A, [1-decene]; B, [2-octyl-1-dodecene]; C, [2-decene].**Figure 7.** Reaction of **4**/MAO with 1-decene at 500 Al/Zr. A, [1-decene]; B, [2-octyl-1-dodecene]; C, [2-decene].**Figure 8.** Reaction of **3**/MAO with 1-decene at 500 Al/Zr. A, [1-decene]; B, [2-octyl-1-dodecene]; C, [2-decene].

octyl-1-dodecene) by measuring the intensities of the olefin resonances in the <sup>1</sup>H NMR spectra.

As shown in Figure 6, **1**/MAO reacts slowly with 1-decene, and approximately 90% of the original 1-decene remains unreacted after 2 h. The error in these measurement is estimated as ±2% from <sup>1</sup>H NMR integration. Figure 7 shows that **4**/MAO reacts more quickly, and that after 1 h, the majority of the 1-decene is converted to 2-decene and 2-octyl-1-dodecene (traces of trimers can also be observed by GC-MS as 1-decene is depleted). Approximately 80% of the 1-decene was dimerized because the end composition corresponds to 67% 2-octyl-1-dodecene and 33% 2-decene and two 1-decene equivalents are required per 2-octyl-1-dodecene equivalent. For **3**/MAO, the reaction profile shows that the rate of 1-decene consumption increases with time (Figure 8). The performance of **10**/MAO is shown in Figure 9 for comparison. Overall, the reluctance to



**Figure 9.** Reaction of **10**/MAO with 1-decene at 500 Al/Zr. A, [1-decene]; B, [2-octyl-1-dodecene]; C, [2-decene].



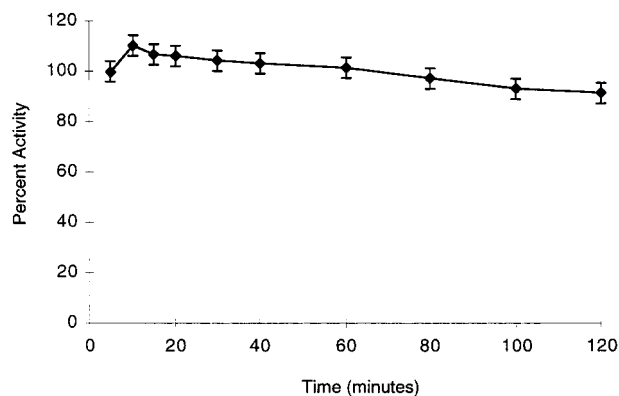
**Figure 10.** Reaction of **1**/MAO and **10**/MAO with 1-decene at 1000 Al/Zr. [1-decene] versus time.

consume 1-decene by **1**/MAO parallels the high specificity for 1-alkenes shown in Table 1.

Higher MAO concentrations increase the rate of 1-decene consumption. This increase is shown in Figure 10, where the percentage 1-decene is plotted against time for reactions of **1**/MAO and **10**/MAO with  $[Al]/[Zr] = 1000$  and  $[Zr] = 5.6 \times 10^{-4}$  M. Note that **1**/MAO remains relatively unreactive and that for **10**/MAO the 1-decene is consumed in less than 20 min.

In a separate experiment, **1**/MAO was reacted with ethylene for 30 min producing a final 1-alkene concentration of approximately 2.5 wt %. The flow of ethylene was terminated and the resulting solution was allowed to stand for an additional hour at 60 °C. After this period approximately 90% of the product remained as 1-alkenes with the remaining 10% present as 1-alkyl-2-alkenes. Only traces of 2-alkenes could be detected.

**Catalyst Lifetime.** The lifetime of metallocene catalysts is an important consideration for their application in polymerization reactions.<sup>30</sup> In many instances catalysts are short-lived but sufficiently active such that the quantity of polymer produced makes them synthetically useful. With these considerations in mind **1**/MAO was tested for activity versus time by using 1000  $[Al]/[Zr]$  and 5  $\mu$ mole of catalyst at 60 °C. The time required to consume a specified volume of ethylene was then measured. Shorter intervals are indicative of more rapid consumption and thus a more active solution. Typically, no induction time was observed and the highest activity was measured at the onset of the reaction. This initial activity was arbitrarily chosen to be 100%. Figure 11 displays the effect of reaction time on the activity of **1**/MAO. Over a period of 2 h, the ethylene



**Figure 11.** Activity of **1**/MAO versus time.

consumption remained at greater than 90% of the initial value. Therefore, the catalytic species from **1**/MAO is robust and only a minor decrease in ethylene uptake occurs, even after extended reaction time.

## Summary Discussion

The clean formation of 1-alkoxyboracyclohexa-2,4-dienes by addition of alcohols to **2**, as shown in eq 1, provides a convenient and flexible approach to various alkoxy-boratabenzene anions. It is interesting that  $PMe_3$  displacement occurs more quickly with neutral alcohols than with stronger nucleophiles, such as  $LiPh$  or  $KPh_2$ .<sup>12</sup> Fu showed that this type of reaction occurs associatively, via a four coordinate boron. Under these conditions the oncoming nucleophile approaches the formally anionic boron atom and the resulting negative charge is distributed on the resulting pentadienyl fragment. We suggest that the faster rates observed with neutral alcohols are a result of a simultaneous protonation at the alpha site of the carbon ring as oxygen approaches boron. No charge buildup occurs, resulting in a lower transition state energy. Similar arguments have been provided by Fu for the increase in rate of substitution on boron upon coordination of **2** to " $Cr(CO)_3$ ".<sup>12</sup>

The general reaction shown by eq 1 works sufficiently well that isolation of the boracyclohexadiene is not required prior to deprotonation. This is an important practical consideration in view of the multistep synthesis of **2**. In addition, it is possible, by use of a suitable diol, to gain access to linked bis-(alkoxyboratabenzene) dianions for design and synthesis of ansa-like zirconium complexes such as **7** and **9**.<sup>31</sup> Complexes **7** and **9** also suggest use of chiral  $C_2$ -symmetric boratabenzene ligands in the design of stereoselective catalysts.

Inspection of Table 1 shows that **1** leads to the catalyst which is least active toward olefins. Consequently, **1**/MAO displays the slowest ethylene uptake and leaves 1-alkenes largely unaffected for long periods of time. Figure 11 shows that the lifetime of **1**/MAO is excellent, with minimal loss of activity observed over a 2 h period at 60 °C. The higher ethylene consumption of other catalysts, such as **4**/MAO or **5**/MAO, could be useful if the 1-alkenes could be removed from the catalyst phase shortly after they are formed.<sup>28</sup>

The results disclosed herein do not allow for an unambiguous identification of the catalytic site. Presumably the mode of activation of MAO is similar to that established in standard metallocenes, namely methylation followed by heterolytic

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(31) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883.



methyl abstraction to leave a cationic complex.<sup>32</sup> The methyl/alkoxide exchange between the boratabenzene boron and trimethylaluminum, as shown in eq 9, raises the possibility that activation of alkoxyboratabenzene precursors with the commercial MAO solutions leads to cationic species of the form  $\{[C_5H_5B-Me]_2Zr-R\}^+$  (R = H or alkyl). The fact that the catalytic properties of **1**/MAO differ from those of **10**/MAO (Figure 6 vs Figure 9) argues that, at least for ethoxy, such an exchange does not take place during the time scale of the oligomerization reaction.<sup>33</sup> For the phenoxy and benzyloxy substituents less is certain because the reactivities of **4**/MAO, **5**/MAO, and **10**/MAO are similar in many ways (Tables 1 and 2 and Figures 7 and 9).

The specificity toward production of 1-alkenes and the lack of decomposition shown by **1**/MAO remains remarkable. This reactivity complements that of other single site catalysts and we recently showed how **1**/MAO in combination with  $[(\eta^5-C_5Me_4SiMe_2(\eta^1-NCMe_3))TiCl_2]^{34}$ /MAO can be used to synthesize branched polyethylene using ethylene alone.<sup>35</sup> An intriguing mechanistic possibility for cationic alkoxy- and aryloxyboratabenzene-based catalysts is that coordination to aluminum by the exocyclic oxygen atom regulates the relative rates of olefin insertion. One should expect, on the basis of steric considerations, that among the boratabenzene ligands studied here the strongest adduct corresponds to the ethoxy group. The presence of a tightly bound AlMe<sub>3</sub> group in the vicinity of the metal may discourage insertion of the larger 1-alkenes relative to ethylene. Unfortunately, given the structural complexity of MAO, a definite account of the role of adduct formation is difficult to obtain. Current efforts are focused on obtaining well-defined catalysts that are amenable to spectroscopic characterization.

## Experimental Section

**General Remarks.** All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques.<sup>36</sup> Phenol and benzyl alcohol were purchased anhydrous from Aldrich Chemical Co., Milwaukee, WI. Cyclohexanol and 1-decene (Aldrich) were dried over molecular sieves 3 Å, degassed, and filtered just prior to use. Racemic *trans*-1,2-cyclohexanediol, trimethylaluminum and racemic binaphthol (Aldrich) were used as received. Toluene, pentane, diethyl ether, and THF were distilled from sodium benzophenone ketyl. Cp\*ZrCl<sub>3</sub>,<sup>37</sup> **1**<sup>38</sup> and **2**<sup>38</sup> were prepared according to literature methods. LDA was prepared from diisopropylamine and *n*-butyllithium at -78 °C. MAO was obtained from Akzo Nobel Chemicals, Inc. NMR spectra were obtained using a Bruker AMX-400 spectrometer. <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra were calibrated using signals from the solvent and are reported downfield from Me<sub>4</sub>Si, whereas <sup>11</sup>B{<sup>1</sup>H} NMR spectra are referenced to external BF<sub>3</sub>·OEt<sub>2</sub>. GC data were collected on a Varian Star 3400 CX Series GC equipped with a flame ionization detector

(32) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(33) There is no change in the catalytic properties of **10**/500 MAO when two equivalents of ethanol are added.

(34) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (c) Lai, S.-Y.; Wilson, S. R.; Knight, G. W.; Stevens, J. C.; Chun, P.-W. S. U.S. Patent 5,272, 236, 1993.

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(37) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

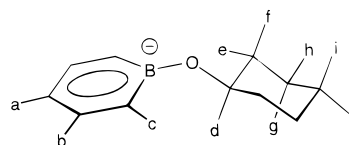
(38) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics*, **1996**, *15*, 1315.

(FID). Elemental analyses were performed by Desert Analytics, Inc., Tucson, AZ.

**General Procedure for Sodium Alkoxyboratabenzenes.** A solution of the alcohol in toluene was added dropwise to a stirred solution of **2** in toluene at room temperature over a 5 min period. The solution was stirred for 1 h and the volatiles were removed in vacuo. The residue was dissolved in THF and added dropwise to a stirred slurry of a slight excess of NaH in THF. After the mixture was stirred for 6–24 h at room temperature the reaction mixture was filtered through Celite and the volatiles were removed in vacuo. The products are obtained as white or cream-colored solids.

**Sodium 1-Cyclohexyloxyboratabenzene.** The general procedure described above was followed using cyclohexanol (108 mg, 1.08 mmol) and **2** (164 mg, 1.08 mmol). Deprotonation was performed using NaH (31 mg, 1.3 mmol) in THF. Solvent removal followed by a pentane wash gave the product as a white, microcrystalline solid, yield: 158 mg, 0.80 mmol, 74%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz): δ 1.27 (m, 4H, g, h, i, or j), 1.54 (m, 2H, g or h), 1.74 (m, 2H, e or f), 1.93 (m, 2H, e or f), 3.91 (m, 1H, d), 5.62 (tt, 1H, a, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 5.66 (dd, 2H, c, <sup>4</sup>J<sub>HH</sub> = 0.9 Hz, <sup>3</sup>J<sub>HH</sub> = 10.4 Hz), 7.13 (dd, 2H, b, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, <sup>3</sup>J<sub>HH</sub> = 10.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 100 MHz): δ 29.2 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 30.2 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 38.9 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 74.5 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 106.4 (CHCHCHB), 114.8 (br, CHCHCHB), 138.4 (CHCHCHB). <sup>11</sup>B{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 128 MHz): δ 39 (br).

Assignment made according to:



**Sodium 1-Phenoxyboratabenzene.** The general procedure described above was followed using phenol (244 mg, 2.59 mmol) and **2** (394 mg, 2.59 mmol). Deprotonation was performed using NaH (83 mg, 3.5 mmol) in THF. The initial isolated yield was 392 mg (2.04 mmol, 79%). The crude product was triturated in 3 mL of Et<sub>2</sub>O for 2 h at room temperature. Filtration and washing with pentane gave the product as an off-white, crystalline solid (280 mg, 56% yield). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz): δ 5.81 (tt, 1H, CHCHCHB, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 5.91 (dd, 2H, CHCHCHB, <sup>4</sup>J<sub>HH</sub> = 0.8 Hz, <sup>3</sup>J<sub>HH</sub> = 10.0 Hz), 6.70 (t, 1H, BOCCHCHCH, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 7.00 (d, 2H, BOCCHCHCH, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.08 (t, 2H, BOCCHCHCH, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 7.20 (dd, 2H, CHCHCHB, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>3</sup>J<sub>HH</sub> = 10.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 100 MHz): δ 108.5 (CHCHCHB), 116.9 (br, CHCHCHB), 122.1 (BOCCHCHCH), 123.3 (BOCCHCHCH), 132.1 (BOCCHCHCH), 132.6 (BOCCHCHCH), 138.3 (CHCHCHB). <sup>11</sup>B{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 128 MHz): δ 39 (br).

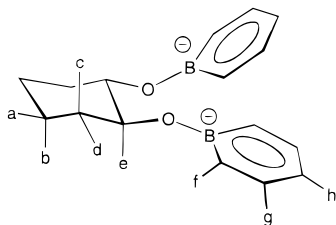
**Sodium 1-Benzyloxyboratabenzene.** The general procedure described above was followed using benzyl alcohol (152 mg, 1.41 mmol) and **2** (214 mg, 1.41 mmol). Deprotonation was performed using NaH (45 mg, 1.9 mmol) in THF. The product was isolated as a white solid (226 mg, 1.10 mmol, 78% yield). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz): δ 4.86 (s, 2H, BOCH<sub>2</sub>), 5.72 (t, 1H, CHCHCHB, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 5.83 (d, 2H, CHCHCHB, <sup>3</sup>J<sub>HH</sub> = 11.2 Hz), 7.10 (t, 1H, BOCH<sub>2</sub>CCHCHCH, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.20 (m, 4H, CHCHCHB and BOCH<sub>2</sub>CCHCHCH), 7.41 (d, 2H, BOCH<sub>2</sub>CCHCHCH, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 100 MHz): δ 70.1 (BOCH<sub>2</sub>), 107.1 (CHCHCHB), 114.5 (br, CHCHCHB), 129.4 (BOCH<sub>2</sub>CCHCHCH), 130.1 (BOCH<sub>2</sub>CCHCHCH), 131.3 (BOCH<sub>2</sub>CCHCHCH), 138.5 (CHCHCHB), 148.0 (BOCH<sub>2</sub>CCHCHCH). <sup>11</sup>B{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 128 MHz): δ 40 (br).

**Synthesis of Na<sub>2</sub>6(THF).** A slurry of *trans*-1,2-cyclohexanediol (117 mg, 1.01 mmol) in 3 mL of toluene was added to **2** (304 mg, 2.00 mmol). After 45 min the reaction became homogeneous. Deprotonation was carried out using NaH (54 mg, 2.25 mmol) in THF. The product was isolated as a white mono-THF adduct (322 mg, 84% yield). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz): δ 1.17 (m, 2H, a or b), 1.40 (m, 2H, a or b), 1.69 (m, 2H, c or d), 1.77 (m, 4H, THF), 2.44 (m, 2H, c or d), 3.62



(m, 4H, THF), 3.83 (m, 2H, e), 5.66 (d, 4H, f,  $^3J_{\text{HH}} = 9.8$  Hz), 5.70 (tt, 2H, h,  $^4J_{\text{HH}} = 1.3$  Hz,  $^3J_{\text{HH}} = 6.9$  Hz), 7.11 (dd, 4H, g,  $^3J_{\text{HH}} = 6.9$  Hz,  $^3J_{\text{HH}} = 10.8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 100 MHz):  $\delta$  28.4 (THF), 28.9 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 36.5 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 70.3 (THF), 80.8 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 108.4 (CHCHCHB), 113.7 (br, CHCHCHB), 139.0 (CHCHCHB).  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF- $d_8$ , 128 MHz):  $\delta$  39 (br).

Assignment made according to:



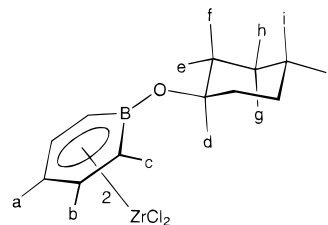
**Synthesis of Li<sub>2</sub>8(THF)<sub>4</sub>.** A slurry of binaphthol (852 mg, 2.97 mmol) in 10 mL of toluene was added to a stirred solution of **2** (904 mg, 5.95 mmol) in 10 mL of toluene over a 10 min period. The solution became homogeneous after it was stirred for an additional 15 min. Precipitation occurred after an additional 30 min of stirring. Following solvent removal, the residue was dissolved in 20 mL of THF and cooled to  $-78$  °C. Under argon purge, a solution of LDA (637 mg, 5.95 mmol) in 6 mL of THF was added via syringe and an immediate color change was observed. The resulting slurry was stirred and allowed to slowly warm to room temperature over a period of 16 h. Removal of volatiles in vacuo afforded the crude product. Purification by trituration in 5 mL of Et<sub>2</sub>O twice followed by filtration gave Li<sub>2</sub>8(THF)<sub>4</sub> as an off-white solid (1.34 g, 61% yield).  $^1\text{H}$  NMR (THF- $d_8$ , 400 MHz):  $\delta$  1.77 (m, 16H, THF), 3.62 (m, 16H, THF), 5.62 (d, 2H, CHCHCHB,  $^3J_{\text{HH}} = 10.9$  Hz), 5.63 (t, 1H, CHCHCHB, under 5.62 ppm peak), 6.88 (dd, 2H, CHCHCHB,  $^3J_{\text{HH}} = 7.3$  Hz,  $^3J_{\text{HH}} = 10.1$  Hz), 7.02 (t, 1H,  $^3J_{\text{HH}} = 7.6$  Hz), 7.15 (m, 2H), 7.71 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 100 MHz):  $\delta$  28.4 (THF), 70.3 (THF), 109.1 (CHCHCHB), 115.8 (br, CHCHCHB), 121.3, 125.2, 127.3, 128.2, 129.4, 129.7, 130.0, 132.7, 136.5 (binaphthyl resonances), 138.0 (CHCHCHB), 158.4 (binaphthyl).  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF- $d_8$ , 128 MHz):  $\delta$  41 (br).

**General Procedure for Bis-Alkoxyboratabenzene Zirconium Dichlorides.** The appropriate stoichiometric amount of sodium or lithium alkoxyboratabenzene and ZrCl<sub>4</sub> were placed in a 100 mL round-bottom flask equipped with a magnetic stir bar. The flask was fitted with a needle valve and was attached to a high-vacuum line. Approximately 20–40 mL of Et<sub>2</sub>O or *n*-heptane was condensed on the solids at  $-78$  °C. The slurry was allowed to warm to room temperature and was stirred over an 8–20 h period. After the reaction was complete, all volatiles were removed in vacuo. The resulting solids were extracted with 10–20 mL of toluene and the extract was filtered through Celite. Removal of volatiles gave golden-yellow to orange-yellow solids of varying purity. Purification of the compounds was performed by trituration in Et<sub>2</sub>O or Et<sub>2</sub>O/pentane followed by filtration through a medium frit. Products were obtained as microcrystalline solids.

**Bis(1-cyclohexyloxyboratabenzene)zirconium Dichloride (3).** The general procedure described was followed using sodium 1-cyclohexyloxyboratabenzene (177 mg, 0.894 mmol) and ZrCl<sub>4</sub> (104 mg, 0.446 mmol). Et<sub>2</sub>O (20 mL) was condensed onto the solids at  $-78$  °C. Under constant stirring the reaction mixture was allowed to warm to room temperature and was stirred for an additional 11 h. Extraction with toluene and isolation gave **3** as a yellow solid (121 mg 53% yield).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.14 (m, 1H, i or j), 1.23 (m, 2H, g or h), 1.41 (m, 1H, i or j), 1.56 (m, 2H, g or h), 1.68 (m, 2H, e or f), 1.94 (m, 2H, e or f), 4.19 (tt, 1H, d,  $^3J_{\text{HH}} = 3.7$  Hz,  $^3J_{\text{HH}} = 9.2$  Hz), 5.68 (dd, 2H, c,  $^4J_{\text{HH}} = 0.9$  Hz,  $^3J_{\text{HH}} = 10.7$  Hz), 5.90 (t, 1H, a,  $^3J_{\text{HH}} = 6.9$  Hz), 7.29 (dd, 2H, b,  $^3J_{\text{HH}} = 6.7$  Hz,  $^3J_{\text{HH}} = 11.1$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  24.2 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.9 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 35.0 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 73.2 (BOCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 104.2 (CHCHCHB), 117.1 (br, CHCHCHB), 147.6 (CHCHCHB).  $^{11}\text{B}\{^1\text{H}\}$  NMR

(C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  34 (br). Anal. Calcd (C<sub>22</sub>H<sub>32</sub>B<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Zr): C, 51.50; H, 6.30. Found: C, 51.88; H, 6.41.

Assignment made according to:



**Bis(1-phenoxyboratabenzene)zirconium Dichloride (4).** The general procedure described above was performed using sodium 1-phenoxyboratabenzene (280 mg, 1.46 mmol) and ZrCl<sub>4</sub> (170 mg, 0.730 mmol). Twenty milliliters of *n*-heptane was condensed onto the solids at  $-78$  °C, and the reaction mixture was stirred at this temperature for 4 h. After this period, the reaction was allowed to warm to room temperature and was stirred for an additional 22 h. Extraction with toluene and filtration gave a green solution. Removal of volatiles gave 168 mg (0.336 mmol, 46% isolated) of the crude product as a yellow-green solid. Trituration in Et<sub>2</sub>O for 2 h and filtration gave pure **4** as a bright yellow solid (114 mg, 31% yield).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  5.76 (dd, 2H, CHCHCHB,  $^4J_{\text{HH}} = 1.6$  Hz,  $^3J_{\text{HH}} = 11.1$  Hz), 5.95 (tt, 1H, CHCHCHB,  $^4J_{\text{HH}} = 1.5$  Hz,  $^3J_{\text{HH}} = 6.8$  Hz), 6.94 (tt, 1H, BOCCHCHCH,  $^4J_{\text{HH}} = 1.6$  Hz,  $^3J_{\text{HH}} = 6.9$  Hz), 7.13 (m, 4H, BOCCHCHCH), 7.20 (dd, 2H, CHCHCHB,  $^3J_{\text{HH}} = 7.0$  Hz,  $^3J_{\text{HH}} = 10.3$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  105.5 (CHCHCHB), 117.7 (br, CHCHCHB), 121.0 (BOCCHCHCH), 123.3 (BOCCHCHCH), 130.0 (BOCCHCHCH), 147.4 (CHCHCHB), 156.3 (BOCCHCHCH).  $^{11}\text{B}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  37 (br). Anal. Calcd (C<sub>22</sub>H<sub>20</sub>B<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Zr): C, 52.83; H, 4.03. Found: C, 53.44; H, 4.24.

**Bis(1-benzyloxyboratabenzene)zirconium Dichloride (5).** The general procedure was followed using sodium 1-benzyloxyboratabenzene (1.31 g, 6.35 mmol) and ZrCl<sub>4</sub> (745 mg, 3.20 mmol). Forty milliliters of Et<sub>2</sub>O was condensed onto the solids at  $-78$  °C and the reaction was stirred for 20 h. Isolation yielded 950 mg (56%) of **5** as a golden-yellow solid.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  5.03 (s, 2H, BOCH<sub>2</sub>), 5.71 (dd, 2H, CHCHCHB,  $^4J_{\text{HH}} = 1.4$  Hz,  $^3J_{\text{HH}} = 10.9$  Hz), 5.92 (tt, 1H, CHCHCHB,  $^4J_{\text{HH}} = 1.3$  Hz,  $^3J_{\text{HH}} = 7.0$  Hz), 7.14 (t, 1H, BOCH<sub>2</sub>CCHCHCH,  $^3J_{\text{HH}} = 7.6$  Hz), 7.25 (m, 4H, CHCHCHB and BOCH<sub>2</sub>CCHCHCH), 7.44 (d, 2H, BOCH<sub>2</sub>CCHCHCH,  $^3J_{\text{HH}} = 7.1$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  67.7 (BOCH<sub>2</sub>), 104.8 (CHCHCHB), 116.9 (br, CHCHCHB), 127.4 (BOCH<sub>2</sub>CCHCHCH), 127.6 (BOCH<sub>2</sub>CCHCHCH), 128.6 (BOCH<sub>2</sub>CCHCHCH), 140.2 (CHCHCHB), 147.6 (BOCH<sub>2</sub>CCHCHCH).  $^{11}\text{B}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  37 (br). Anal. Calcd (C<sub>24</sub>H<sub>24</sub>B<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Zr): C, 54.57; H, 4.58; Found: C, 54.37; H, 4.64.

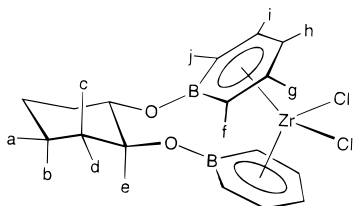
**Synthesis of 7.** The general procedure described above was followed using Na<sub>2</sub>6(THF) (311 mg, 0.997 mmol) and ZrCl<sub>4</sub> (232 mg, 0.996 mmol). Fifty milliliters of Et<sub>2</sub>O was condensed onto the solids at  $-78$  °C. The solution was allowed to warm to room temperature and was stirred for an additional 18 h. Extraction and isolation gave 150 mg (35% yield) of **7** as a yellow microcrystalline solid.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.04 (m, 2H, a or b), 1.29 (m, 2H, a or b), 1.49 (m, 2H, c or d), 1.92 (m, 2H, c or d), 4.03 (m, 2H, e), 5.20 (ddd, 2H, f,  $^4J_{\text{HH}} = 1.6$  Hz,  $^4J_{\text{HH}} = 3.1$  Hz,  $^3J_{\text{HH}} = 10.9$  Hz), 5.96 (ddd, 2H, j,  $^4J_{\text{HH}} = 1.4$  Hz,  $^4J_{\text{HH}} = 3.1$  Hz,  $^3J_{\text{HH}} = 11.4$  Hz), 6.39 (tt, 2H, h,  $^4J_{\text{HH}} = 1.4$  Hz,  $^3J_{\text{HH}} = 6.9$  Hz), 7.04 (ddd, 2H, g,  $^4J_{\text{HH}} = 2.2$  Hz,  $^3J_{\text{HH}} = 6.7$  Hz,  $^3J_{\text{HH}} = 11.2$  Hz), 7.71 (ddd, 2H, i,  $^4J_{\text{HH}} = 2.2$  Hz,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HH}} = 10.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  24.4 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 33.6 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 78.2 (BOCHCH<sub>2</sub>CH<sub>2</sub>), 111.9 (CHCHCHB), 112.8 (br, CHCHCHB), 119.6 (br, CHCHCHB), 145.0 (CHCHCHB), 155.6 (CHCHCHB).  $^{11}\text{B}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  36 (br). Anal. Calcd (C<sub>16</sub>H<sub>20</sub>B<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Zr): C, 44.89; H, 4.71. Found: C, 45.03; H, 4.66.

**Table 3.** Summary of Crystallographic Data for **4** and **7**

crystal parameters	<b>4</b>	<b>7</b>
chemical formula	C <sub>22</sub> H <sub>20</sub> B <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub> Zr	C <sub>21</sub> H <sub>32</sub> B <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub> Zr
formula weight	500.12	500.21
crystal system	monoclinic	monoclinic
space group (no.)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>C</i> 2/ <i>c</i> (15)
<i>Z</i>	4	8
<i>a</i> , Å	15.2654(3)	18.5883(4)
<i>b</i> , Å	6.6931(1)	13.5596(3)
<i>c</i> , Å	21.0237(2)	16.6153(4)
$\beta$ , deg	104.363(1)	105.860(1)
volume, Å <sup>3</sup>	2080.91(6)	4028.5(2)
$\rho_{\text{calc}}$ , mg·mm <sup>-3</sup>	1.596	1.649
cryst. dimens., mm <sup>3</sup>	0.16 × 0.08 × 0.06	0.20 × 0.18 × 0.18
temp., °C	-80	-80
measurement of intensity data and refinement parameters		
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.71073)	
2 $\theta$ range, deg	4-56.6	4-46.5
data collected	-14 ≤ <i>h</i> ≤ 20, -8 ≤ <i>k</i> ≤ 7, -27 ≤ <i>l</i> ≤ 27	-20 ≤ <i>h</i> ≤ 20, -15 ≤ <i>k</i> ≤ 9, -17 ≤ <i>l</i> ≤ 18
no. of data collected	11 604	8194
no. of unique data	4756	2822
<i>R</i> <sub>int</sub> , <i>R</i> <sub>sigma</sub> (%) <sup>a</sup>	3.36, 5.08	5.70, 6.31
no. obs. data ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3719	2172
no. parameters varied	262	228
$\mu$ , mm <sup>-1</sup>	0.802	0.827
absorption correction	empirical (SADABS)	
range of trans. factors	0.842-0.928	0.537-0.928
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> ), <i>wR</i> <sub>2</sub> ( <i>F</i> )	4.32, 6.80	6.77, 17.42
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> ), <i>wR</i> <sub>2</sub> ( <i>F</i> )	6.67, 7.42	8.58, 18.66

<sup>a</sup>  $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$ ;  $R_{\text{sigma}} = \sum [\sigma(F_o^2)] / \sum [F_o^2]$ . <sup>b</sup>  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$  and  $P = [(Max; O, F_o^2) + 2 \cdot F_c^2] / 3$ .

Assignment made according to



**Synthesis of 9.** The general procedure described above was performed using Li<sub>2</sub>8(THF)<sub>4</sub> (1.35 g, 1.82 mmol) and ZrCl<sub>4</sub> (424 mg, 1.82 mmol). Forty milliliters of Et<sub>2</sub>O was condensed onto the solids at -78 °C and the reaction mixture was allowed to warm to room temperature and was stirred for 17 h. Extraction with toluene and filtration gave an orange-yellow solution. Removal of volatiles gave 702 mg (64%) of **9** as an orange-yellow solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  5.12 (ddd, 2H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.5 Hz), 5.66 (ddd, 2H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.0 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.2 Hz), 6.33 (tt, 2H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz), 6.96 (tt, 2H, binaphthyl, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz), 7.02 (m, 2H, binaphthyl), 7.11 (d, 2H, binaphthyl, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz), 7.17 (m, 2H, CHCHCHB, overlaps with C<sub>6</sub>HD<sub>5</sub> resonance), 7.46 (d, 2H, binaphthyl, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz), 7.60 (ddd, 2H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 2.7 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.4 Hz), 7.63 (d, 2H, binaphthyl, <sup>3</sup>*J*<sub>HH</sub> = 9.0 Hz), 7.72 (d, 2H, binaphthyl, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  110.0 (CHCHCHB), 113.4 (br, CHCHCHB), 115.7 (br, CHCHCHB), 121.2, 122.1, 124.6, 125.7, 126.8, 127.0, 129.3, 130.8, 134.7 (binaphthyl resonances), 149.0 (CHCHCHB), 152.3 (binaphthyl), 156.2 (CHCHCHB). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  36 (br). Anal. Calcd (C<sub>30</sub>H<sub>22</sub>B<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Zr): C, 44.89; H, 4.71. Found: C, 45.03; H, 4.66.

**Synthesis of Cp\*[C<sub>5</sub>H<sub>5</sub>B-OEt]ZrCl<sub>2</sub> (**11**).** A solution of sodium 1-ethoxyboratabenzene (144 mg, 1.01 mmol) in 3 mL of THF and a slurry of Cp\*ZrCl<sub>3</sub> (333 mg, 1.00 mmol) in 3 mL of Et<sub>2</sub>O were cooled to -35 °C. Addition of the 1-ethoxyboratabenzene solution to Cp\*ZrCl<sub>3</sub> was carried out over a 10 min period under constant stirring. Volatiles were removed in vacuo. Toluene extraction and filtration gave a light yellow solution. Removal of toluene gave 321 mg (77% yield) of **11**

as a yellow crystalline solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.34 (t, 3H, BOCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz), 1.74 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 4.14 (q, 2H, BOCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz), 5.21 (tt, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.7 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz), 5.71 (dd, 2H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.6 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.1 Hz), 7.00 (dd, 2H, CHCHCHB, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.1 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  12.5 (BOCH<sub>2</sub>CH<sub>3</sub>), 17.6 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 60.8 (BOCH<sub>2</sub>CH<sub>3</sub>), 100.7 (CHCHCHB), 116.2 (br, CHCHCHB), 125.6 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 145.5 (CHCHCHB). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  37 (br). Anal. Calcd (C<sub>17</sub>H<sub>25</sub>BCl<sub>2</sub>OZr): C, 48.81; H, 6.02. Found: C, 48.66; H, 5.97.

**Cp\*[C<sub>5</sub>H<sub>5</sub>B(OEt)(AlMe<sub>3</sub>)]ZrCl<sub>2</sub> (**12**).** To a slurry of **11** (20 mg, 48  $\mu$ mole) in 3 mL of a 50:50 toluene/pentane mixture was added a few drops of (AlMe<sub>3</sub>)<sub>2</sub> (excess). The resulting slurry was filtered and cooled to -35 °C for 2 weeks and fine yellow needles of the product formed. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  -0.43 (s, 9H, Al(CH<sub>3</sub>)<sub>3</sub>), 0.91 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz), 1.69 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 3.36 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz), 5.63 (tt, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz), 5.68 (ddd, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.7 Hz, <sup>4</sup>*J*<sub>HH</sub> = 2.8 Hz, <sup>3</sup>*J*<sub>HH</sub> = 10.5 Hz), 6.42 (ddd, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.7 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, <sup>3</sup>*J*<sub>HH</sub> = 10.5 Hz), 6.56 (ddd, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, <sup>3</sup>*J*<sub>HH</sub> = 10.5 Hz), 7.08 (ddd, 1H, CHCHCHB, <sup>4</sup>*J*<sub>HH</sub> = 1.8 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz, <sup>3</sup>*J*<sub>HH</sub> = 10.7 Hz). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz):  $\delta$  38 (br). Thermal instability precludes elemental analysis and <sup>13</sup>C NMR spectroscopy.

**Ethylene Oligomerization Procedure.** In a glovebox, stock solutions of the precatalysts were prepared by placing known amounts in a vial and bringing the concentration to 5.00  $\mu$ mole/g of toluene solution. A 1.00 g fraction of this solution was combined with the appropriate amount of MAO, 9.6 wt % aluminum (1000 equiv of Al = 1.405 g = 5.00 mmol). Immediately after addition a color change to a deeper yellow or orange was observed. The resulting solution was placed inside a 100 mL round-bottom flask equipped with a stir bar, and an additional 40 mL of toluene was added. The flask was fitted with a needle valve and was removed from the glovebox. The mass of the entire assembly was recorded to the nearest 0.01 g, and the assembly was attached to a vacuum line. The flask was partially evacuated for 15-30 s and brought to 60 °C. After 30 min of exposure to 1 atm ethylene, the assembly was reweighed to the nearest 0.01 g. The reaction was quenched using 3 mL of water and the resulting aluminum-

**Table 4.** Summary of Crystallographic Data for **11** and **12**

crystal parameters	<b>11</b>	<b>12</b>
chemical formula	C <sub>17</sub> H <sub>25</sub> BCl <sub>2</sub> OZr	C <sub>20</sub> H <sub>34</sub> AlBCl <sub>2</sub> OZr
formula weight	418.30	490.38
crystal system	monoclinic	orthorhombic
space group (no.)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	<i>Pbca</i> (61)
<i>Z</i>	8	8
<i>a</i> , Å	13.009(2)	22.7388(3)
<i>b</i> , Å	18.101(3)	8.9836(1)
<i>c</i> , Å	15.908(2)	23.3353(1)
$\beta$ , deg	90.68(1)	
volume, Å <sup>3</sup>	3745.7(10)	4766.85(8)
$\rho_{\text{calc}}$ , mg·mm <sup>-3</sup>	1.484	1.367
cryst. dimens., mm <sup>3</sup>	0.28 × 0.18 × 0.02	0.28 × 0.24 × 0.16
temp., °C	-80	-80
measurement of intensity data and refinement parameters		
radiation ( $\lambda$ , Å)	MoK $\alpha$ (0.71073)	
2 $\theta$ range, deg	3–46.5	3–56.6
data collected	-14 ≤ <i>h</i> ≤ 14, -20 ≤ <i>k</i> ≤ 16, -17 ≤ <i>l</i> ≤ 17	-30 ≤ <i>h</i> ≤ 26, -11 ≤ <i>k</i> ≤ 11, -22 ≤ <i>l</i> ≤ 31
no. of data collected	16 446	27 052
no. of unique data	5360	5772
<i>R</i> <sub>int</sub> , <i>R</i> <sub>sigma</sub> (%) <sup>a</sup>	4.39, 4.84	3.37, 2.83
no. obs. data ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4201	5072
no. parameters varied	409	244
$\mu$ , mm <sup>-1</sup>	0.871	0.729
absorption correction	empirical (SADABS)	
range of trans. factors	0.736–0.928	0.711–0.928
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> ), <i>wR</i> <sub>2</sub> ( <i>F</i> )	3.65, 7.59	4.28, 8.14
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> ), <i>wR</i> <sub>2</sub> ( <i>F</i> )	5.60, 8.39	5.47, 8.54

<sup>a</sup>  $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$ ;  $R_{\text{sigma}} = \sum [\sigma(F_o^2)] / \sum [F_o^2]$ . <sup>b</sup>  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1 / [\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$  and  $P = [(Max; O, F_o^2) + 2 \cdot F_c^2] / 3$ .

containing salts were dissolved in aqueous base. The toluene layer was isolated and analyzed using <sup>1</sup>H NMR spectroscopy, GC and GC–MS.

**1-Decene Isomerization.** Fifteen  $\mu$ moles of the precatalyst was combined with either 500 or 1000 equiv of MAO, diluted with 20 mL of toluene, and placed inside a three-neck, 100 mL round-bottom flask fitted with two rubber septa. The flask was fitted with a needle valve and the assembly attached to a vacuum line. The flask was kept at room temperature using an external water bath. Under argon purge, 5.0 mL of 1-decene was added to the reaction flask and the initial time was recorded. The reaction mixture was stirred at room temperature, and 0.8 mL aliquots were withdrawn at various times using a syringe and then were immediately quenched with water. The mixtures were then diluted with 1 mL of cyclohexane, dried with anhydrous MgSO<sub>4</sub>, and filtered.

**Catalyst Lifetime.** A solution of 1/MAO (5.00  $\mu$ mole Zr, [Al]/[Zr] = 1000) was used to oligomerize ethylene at 60 °C for 2 h. Ethylene uptake was recorded by measuring the time required for a given volume to be consumed by use of an oil bubbler. The reciprocal of this quantity is proportional to the activity of the catalyst and this value was adjusted to be an arbitrary 100% at the onset of the oligomerization.

**Structure Determination for 4, 7, 11, and 12.** The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in  $\omega$  and exposure times of either 30 s/frame (**7** and **12**) or 60 s/frame (**4** and **11**) using a detector-to-crystal distance of 5.09 cm (maximum 2 $\theta$  angle of 56.6°). The total data collection time was approximately either 12 or 25 h, respectively, for 30 or 60 s frames. Frames were integrated to 0.90 Å for **7** and **11** and 0.75 Å for **4** and **12** with the Siemens SAINT program. Laue symmetry revealed monoclinic crystal systems for **4**, **7**, and **11** and an orthorhombic crystal system for **12**, and the final unit cell parameters (at -80 °C) were determined from the least-squares refinement of three-dimensional

centroids of >4500 reflections for all of the crystals except **11**.<sup>39</sup> Data were corrected for absorption with the SADABS<sup>40</sup> program.

The space group assignments are provided in Tables 3 and 4. A molecule of pentane is found in the lattice of **7**. The structures were solved by using direct methods and refined employing full-matrix least-squares on *F*<sup>2</sup> (Siemens, SHELXTL,<sup>41</sup> version 5.04). All of the non-H atoms of the molecular species were refined anisotropically for all of the data sets, and the hydrogen atoms were included in idealized positions. The final residuals are provided in Tables 3 and 4. Goodness of fit (GOF) values ranged between 0.980 and 1.143. Further details of the data collection, solution, and refinement can be found in the Supporting Information.

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**Supporting Information Available:** Complete details for the synthesis, reactivity and X-ray crystallographic studies of **4**, **7**, **11**, and **12** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(39) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, because systematic error is not included. More reasonable errors might be estimated at 10× the listed value. It should be noted that the SAINT program could not improve the original cell produced by SMART for **11**, and hence the final unit cell is based upon only 168 reflections.

(40) The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(41) SHELXTL: *Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc.: Madison, WI, 1995.