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^{11}B NMR Analysis of Catalyst Solutions Obtained from Bis(boratabenzene)zirconium Dichloride Complexes and Methylaluminoxane

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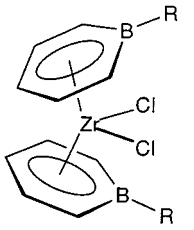
Boratabenzene complexes of the type [C$_5$H$_5$B-R]$_2$ZrCl$_2$ are activated by methylaluminoxane (MAO) to form catalyst mixtures that polymerize (R = dialkylamino) or oligomerize (R = alkyl, alkoxy) ethylene. The selectivity for specific olefin products is influenced by the exocyclic substituent on the boratabenzene ring. When [C$_5$H$_5$B-OEt]$_2$ZrCl$_2$(**1**)/MAO is exposed to 1 atm of ethylene, α-olefins are produced in greater than 99% purity, while [C$_5$H$_5$B-Me]$_2$ZrCl$_2$(**4**)/MAO/C$_2$H$_4$ gives a mixture of α-olefins, internal olefins, and vinylidenes. Other catalysts, such as [C$_5$H$_5$B-OCH$_2$Ph]$_2$ZrCl$_2$(**2**)/MAO and [C$_5$H$_5$B-OCy]$_2$ZrCl$_2$(**3**)/MAO, oligomerize ethylene with selectivities for α-olefin production that are between those of **1**/MAO and **4**/MAO. The isomerization and dimerization of 1-decene by **1**−**4** with MAO agree well with the ethylene data. More selective catalysts (**1**/MAO) exhibit slow rates of isomerization, while less selective catalysts (**4**/MAO) rapidly convert 1-decene to 2-decene and 2-octyl-1-dodecene. The presence of boron in the ancillary ligands of these catalyst mixtures allows their reaction chemistry to be examined using ^{11}B NMR spectroscopy. Signals are observed at 35 and 42 ppm for **1**/MAO and **4**/MAO, respectively. These signals remain unchanged over a 3 h period. For **2**/MAO the initial resonance at 35 ppm diminishes with time and gives rise to a signal at 42 ppm. Two new zirconium complexes, [C$_5$H$_5$B-OMe]$_2$ZrCl$_2$(**5**)/MAO and [C$_5$H$_5$B-OCMe$_3$]$_2$ZrCl$_2$(**6**)/MAO, were synthesized to further examine steric effects. With **5**/MAO, no exchange was observed. A rapid exchange of exocyclic substituent occurs for **6**/MAO. Ethylene oligomerization and 1-decene isomerization reactions with **5**/MAO and **6**/MAO support these observations. Different commercially available samples of MAO were also compared.

Introduction

Boratabenzene complexes[1] of the type [C$_5$H$_5$B-R]$_2$ZrCl$_2$ (R = alkyl, alkoxy, dialkylamino) can be activated with large excesses of methylaluminoxane[2] (MAO) to form catalysts that polymerize or oligomerize ethylene.[3] The olefin consumption activity and selectivity for production of α-olefins of these catalysts vary with the nature of the exocyclic group.[4] For example, when exposed to 1 atm of ethylene, [C$_5$H$_5$B-N(^{i}Pr)$_2$]$_2$ZrCl$_2$/MAO produces polyethylene with activities comparable to those of group 4 metallocenes.[5] Under similar conditions, [C$_5$H$_5$B-OEt]$_2$ZrCl$_2$/MAO (**1**) gives 1-alkenes in greater than 99% purity, with a comparable rate of ethylene consumption.[6] The catalyst produced by **1**/MAO maintains the rapid rate of ethylene insertion characteristic of activated group 4 metallocenes but displays a faster rate of β-hydrogen elimination and a reluctance to react with 1-alkenes once they form.



1, R = OEt
2, R = OCH$_2$Ph
3, R = OCy
4, R = Me

The importance of 1-alkenes in the chemical industry[7] led us to investigate the selectivity observed with **1**/MAO in more detail. The closely related *alkoxy*boratabenzene analogues [C$_5$H$_5$B-OCH$_2$Ph]$_2$ZrCl$_2$ (**2**) and [C$_5$H$_5$B-OCy]$_2$ZrCl$_2$ (**3**) and the *methyl*boratabenzene

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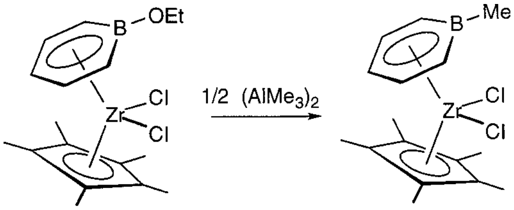
derivative $[C_5H_5B\text{-}Me]_2ZrCl_2$ (**4**)[8] display poor selectivity and give mixtures of 1-alkenes, 2-alkenes, and 2-alkyl-1-alkenes (1-alkene dimers). Exchange reactions between the boratabenzene boron and aluminum are also known, giving uncertainty as to the nature of the boron substituent during the catalytic process. For example, as shown in eq 1, when $(AlMe_3)_2$ is reacted with



(1)

$Cp^*[C_5H_5B\text{-}OEt]ZrCl_2$, one obtains $Cp^*[C_5H_5B\text{-}Me]ZrCl_2$ cleanly.[9] Since commercially available sources of MAO contain varying amounts of trimethylaluminum,[2a,b] this exchange raises the possibility that the electronic effects of the boratabenzene ligand change over time.[10]

A well-known drawback associated with MAO is the difficulty in observing the active species by NMR spectroscopy.[11−13] This is due in part to the very large Al/M ratios required for the formation of an active species and to the poorly defined structure of MAO.[14−18] Furthermore, the MAO structure depends on the process by which trimethylaluminum is hydrolyzed and can change by standing over time.[2a,15,19] The presence of a unique heteroatom in the ancillary boratabenzene ligand makes these complexes attractive study subjects for analysis using ^{11}B NMR spectroscopy by monitoring changes in the spectrum with reaction time.[20] Additionally, the resonances of these complexes depend on the boron substituent and are thus useful in monitoring exchange reactions.

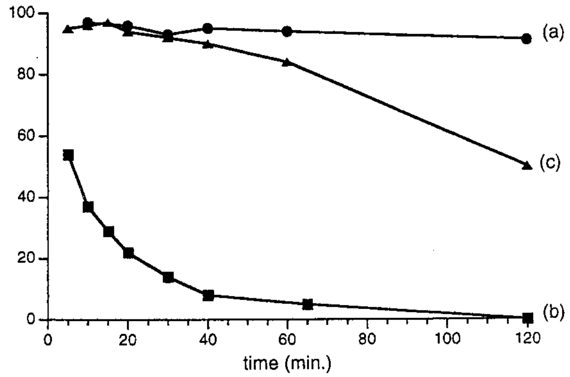


Figure 1. Isomerization of 1-decene by (a) **1**/MAO, (b) **4**/MAO, and (c) **3**/MAO in toluene. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C, [1-decene] = 1.0 M.

In this contribution we probe the structure of a catalytic species such as **1**/MAO by using ^{11}B NMR spectroscopy with the intent of characterizing the heterogeneity of active sites and boron/aluminum transmetalation reactions. Since the chemical structure and reactivity of MAO are variable,[2a,16,21] we also compare the catalytic properties as a function of two commercially available MAO products. Our goal is to determine the structural attributes of highly selective oligomerization catalysts to further optimize their performance.

Results and Discussion

Experimental Conditions. We have previously shown a relationship between the selectivity toward 1-alkene formation from ethylene and the rate at which boratabenzene catalysts isomerize and dimerize 1-decene to 2-decene and 2-octyl-1-dodecene, respectively.[9] In the ethylene reactions, the 1-alkene product forms first. A review of these studies is necessary to place the NMR results in context. Figure 1 shows the rates at which 1-decene is consumed as a function of precatalyst structure. Complete details for these experiments can be found in ref 9. For **1**/MAO (Figure 1a) the concentration of 1-decene remains essentially unchanged, even after 2 h of reaction. In contrast, a sharp decline takes place in the presence of **4**/MAO (Figure 1b). A large fraction of 1-decene has been consumed by the time the first measurement is taken (~5 min). With the cyclohexyloxy-substituted system **3**/MAO, an initial slow consumption of 1-decene takes place, resembling the profile of **1**/MAO. The rate of consumption, however, accelerates with time (Figure 1c), suggesting the formation of a catalyst that would be less selective for producing 1-alkenes from ethylene.

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(12) Group 4 metallocene/MAO mixtures have been studied by FTIR; see: Eilertsen, J. L.; Rytter, E.; Ystenes, M. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, Heidelberg, 2001; p 86.

(13) UV/vis spectroscopic studies on group 4 metallocene/MAO mixtures has been carried out; see: Wieser, U.; Brintzinger, H.-H. *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, Heidelberg, 2001; p 3.

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(18) MAO structures have been probed using EPR techniques; see: Talsi, E. P.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Babushkin, D. E.; Shubin, A. A.; Zakharov, V. A. *J. Mol. Catal. A* **1999**, *139*, 131.

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(20) Activation of group 4 metallocenes with MAO has been studied by ^{91}Zr NMR spectroscopy; see: Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Schroepfer, J. N. *J. Mol. Catal. A* **1998**, *128*, 257.

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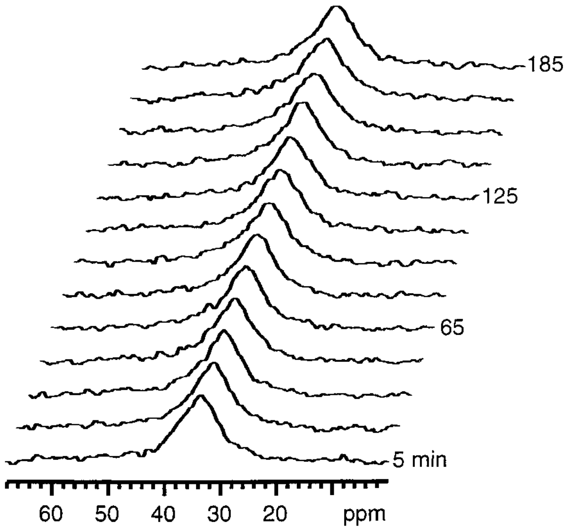

Figure 2. ^{11}B NMR of **1**/MAO versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

The conditions for measuring ^{11}B NMR spectra were chosen to be identical with those optimized for following 1-decene isomerizations ($[Zr] = 5 \times 10^{-4}$ M, Al/Zr = 500, 23 °C, [1-decene] = 1.0 M in toluene). To compensate for the low metal concentration, 10 mm quartz NMR tubes were used. Borosilicate tubes were not satisfactory, because they gave a rolling baseline when probing the ^{11}B nucleus. Because ^{11}B is a quadrupolar nucleus and produces broad signals, shimming the magnet is not necessary and no deuterated solvent (to obtain a lock) was used. A line broadening of 100, used to improve signal to noise, did not result in a significant change in signal line shape. All spectra were referenced externally to neat $BF_3{\cdot}Et_2O$.

Effect of the Boron Substituent on Transmetalation Rates. Figure 2 shows the ^{11}B NMR spectra corresponding to **1**/MAO over a 3 h period. A broad peak centered at 35 ppm is observed which does not change over the duration of the experiment and, by integration against an external standard, may be assigned to the majority of the boron-containing species (>80%). Minor peaks (<5%) downfield of the major peak (72 and 89 ppm) develop over time, which are indicative of vinyldialkylborane and trialkylborane, respectively. These are attributed to decomposition of the boratabenzene ligand. The spectra corresponding to **4**/MAO are shown in Figure 3. A broad resonance at 42 ppm is observed, which remains unchanged throughout the duration of the reaction. As with the **1**/MAO combination, **4**/MAO shows some decomposition of the boratabenzene ligand with time.

It is interesting that the signals from **1**/MAO and **4**/MAO in toluene are quite similar to those of the corresponding MAO-free compounds **1** (34 ppm) and **4** (45 ppm).[22,23] One might initially expect significant downfield shifts upon the addition of MAO and the generation of a more electron deficient zirconium.[11,24–26] However, it is known that addition of $Cp^*[C_5H_5B\text{-}Me]ZrMe_2$ to $B(C_6F_5)_3$ results in $[Cp^*[C_5H_5B\text{-}Me]ZrMe][MeB(C_6F_5)_3]$. This reaction gives rise to only minor changes in chemical shift for the boratabenzene boron (from 42 to 47 ppm), while the tris(perfluoroaryl)-substituted boron exhibits a much larger upfield shift (from 60 to −14 ppm).[10b] Incomplete activation of the zirconium sites cannot be ruled out.

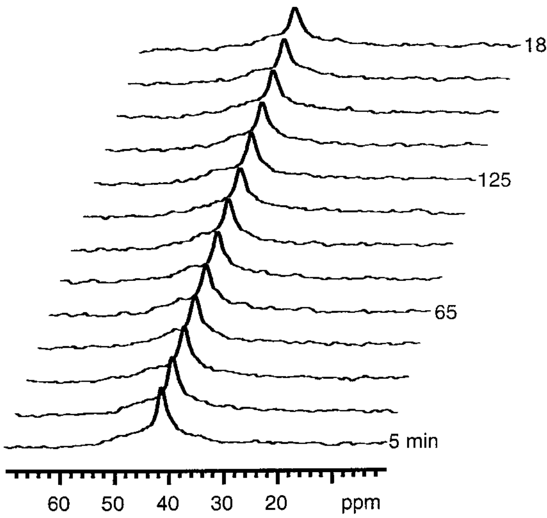

Figure 3. ^{11}B NMR of **4**/MAO versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

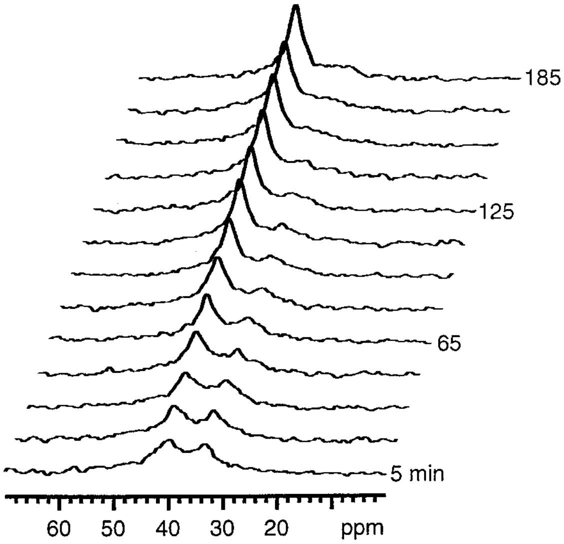

Figure 4. ^{11}B NMR of **2**/MAO versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

Comparison of Figures 2 and 3 demonstrates that in the case of the ethoxyboratabenzene ligand the presence of MAO does not give rise to methylboratabenzene structures. These data also support the idea that these two reaction mixtures contain chemically different active sites. Monitoring the reactions of **1**/MAO and **4**/MAO in the presence of 1-decene results in the same ^{11}B NMR signals.

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[22] These values were obtained by dissolving the corresponding zirconium species in toluene and acquiring the ^{11}B spectrum, referenced externally to $BF_3{\cdot}Et_2O$.

[23] These numbers match well other resonance assignments in the literature. See: Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751.

[24] Coevoet, D.; Cramail, H.; Deffieux, A.; Mladenov, C.; Pedeutour, J.-N.; Peruch, F. *Polym. Int.* **1999**, *48*, 257.

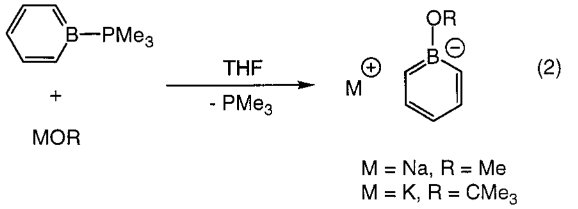
[25] Pedeutour, J.-N.; Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1999**, *200*, 1215.

[26] These systems have been modeled using DFT calculations; see: Fusco, R.; Longo, L.; Masi, F.; Garbassi, F. *Macromolecules* **1997**, *30*, 7673.

Figure 4 shows the ^{11}B NMR spectra of **2**/MAO over a 3 h period. Within 5 min, the time required for measuring the first spectrum, two peaks are observed at 35 and 42 ppm. As time progresses, the signal at 42 ppm gains intensity at the expense of the upfield signal. The similarity of the signal at 42 ppm to the spectrum of **4**/MAO suggests that the boron substituent changes from benzyloxy to methyl over time. Unfortunately, despite repeated attempts to optimize the samples and data collection parameters, the ^{11}B NMR spectra of **3**/MAO are too broad to be diagnostic.

Altogether, the data in Figures 2–4 indicate that B/Al exchange reactions are favored with bulkier alkoxides. The smaller ethoxy group of **1** is the most resistant to exchange. Signals that could be attributed to methylboratabenzene species are only observed at higher concentrations and after 3 h of reaction ([Zr] = 2.5 × 10^{-3} M, Al:Zr = 500) (Figure 5).

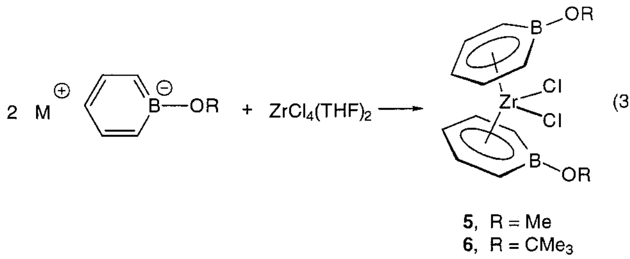
Methoxyboratabenzene and *tert*-Butoxyboratabenzene Complexes. To further examine steric effects, we prepared $[C_5H_5B\text{-}OMe]_2ZrCl_2$ (**5**) and $[C_5H_5B\text{-}OCMe_3]_2ZrCl_2$ (**6**). Sodium methoxyboratabenzene was obtained by the addition of sodium methoxide to $C_5H_5B\text{-}PMe_3$ in THF, according to the method of Fu (eq 2).[27]



(2)

For the *tert*-butoxy group, the potassium alkoxide was used because it was more readily available.

Addition of 2 equiv of ligand salt to $ZrCl_4(THF)_2$ in Et_2O or THF affords the desired complexes **5** and **6** as golden yellow solids (eq 3).



(3)

Ethylene oligomerizations carried out with **5**/MAO ([Zr] = 5 × 10^{-4} M in toluene, Al:Zr = 500, 22 °C, $P(C_2H_4)$ = 1.0 atm) give rise to the lowest activity observed for any alkoxyboratabenzene based catalyst (250 kg of product/((mol of Zr) h)). The product, however, contains 98% 1-alkenes, with the remainder consisting of 2-alkenes. The overall low activity and high α-olefin selectivity found using **5**/MAO are similar to those obtained using **1**/MAO (325 kg of product/((mol of Zr) h)), under identical reaction conditions. The results of oligomerization using **6**/MAO follow those of the less selective alkoxyboratabenzene catalysts, giving only 66% 1-alkenes under the same conditions. The other olefin products are 2-alkyl-1-alkenes (19%) and 2-alkenes (15%). The reactivity of the **6**/MAO combination is similar to that of $(C_5H_5B\text{-}OCy)_2ZrCl_2$/MAO and has an activity of 680 kg of product/((mol of Zr) h).

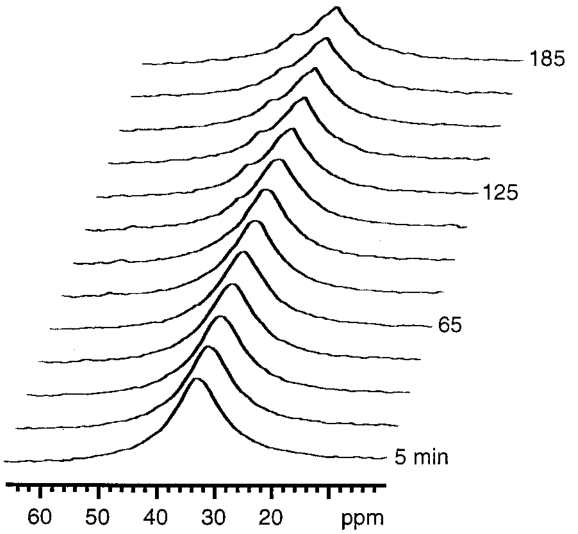


Figure 5. ^{11}B NMR of **1**/MAO versus time. Conditions: [Zr] = 2.5 × 10^{-3} M, Al:Zr = 500, 23 °C.

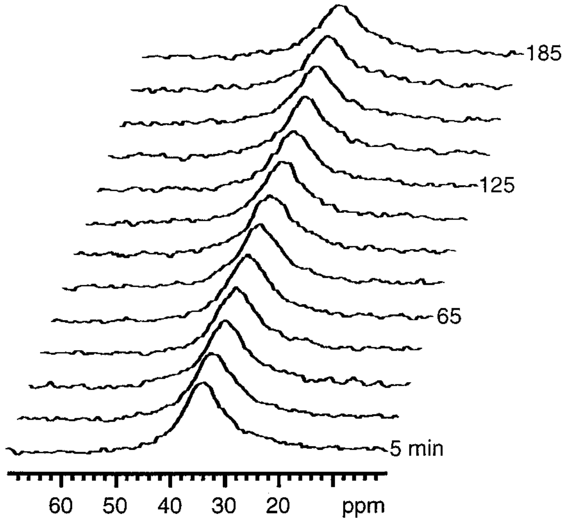


Figure 6. ^{11}B NMR of **5**/MAO versus time. Conditions: [Zr] = 5 × 10^{-4} M, Al:Zr = 500, 23 °C.

Monitoring **5**/MAO and **6**/MAO by ^{11}B NMR spectroscopy supports previous trends. The **5**/MAO combination displays a broad resonance centered at 35 ppm (Figure 6), which remains unchanged throughout the experiment. Figure 7 shows the ^{11}B spectra of **6**/MAO under identical conditions. The change in chemical shift from 35 to 42 ppm suggests an exchange of boron substituent to a B-Me functionality, similar to the process observed with **2**/MAO.

Methylaluminoxane Source. Measuring the ^{11}B NMR signal of boratabenzene complexes provides a convenient method for examining how MAO samples impact the structure of the organometallic species in solution. Since manufacturers rely on various preparation methods, which affect the final MAO structure,[2a,14] the metal complexes may have different reactivities with choice of MAO source.[21] The isomerization of 1-decene by **5**/MAO was carried out with two commercially available MAO sources: Akzo Nobel Chemicals (MAOa),

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[27] Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329.

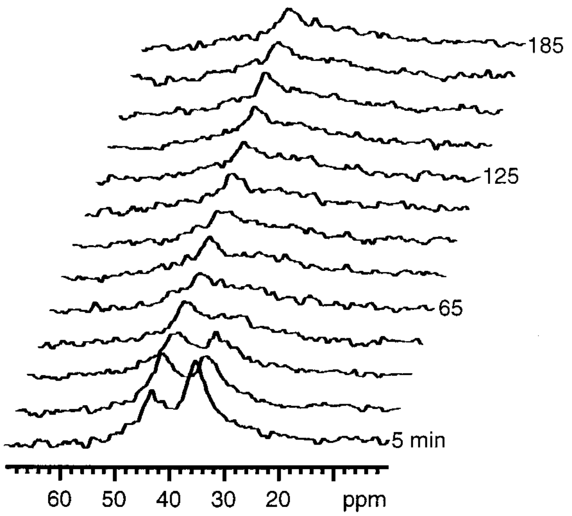

Figure 7. ^{11}B NMR of **6**/MAO versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

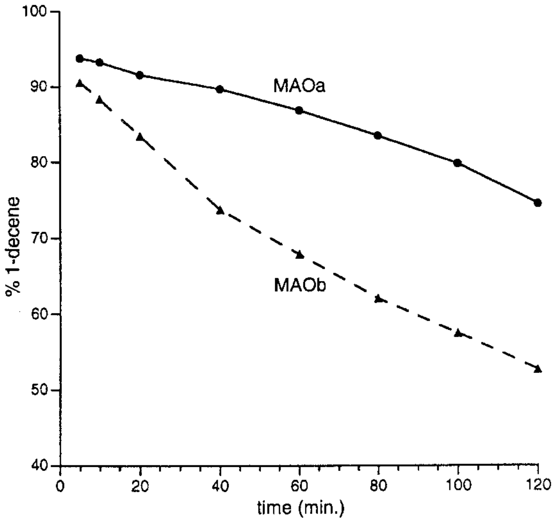

Figure 8. Isomerization of 1-decene by **5** with MAOa (Akzo) and MAOb (Albemarle). Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C, [1-decene] = 1.0 M in toluene.

which was used for all prior experiments, and Albemarle Corp. (MAOb).

Precatalyst **5** was combined with MAOa and MAOb in separate 1-decene isomerization experiments. The results of these experiments are shown in Figure 8 and demonstrate a faster rate of isomerization with **5**/MAOb. Ethylene oligomerizations carried out with **5** and both cocatalysts provides complementary information. Previously, it was shown that **5**/MAOa gives 98% selectivity toward the preparation of 1-alkenes (vide supra). The same reaction using **5**/MAOb results in lower selectivity (90%) for 1-alkenes and a concomitant increase in activity (440 kg of product/((mol of Zr) h)). This combination (**5**/MAOb) was also studied by ^{11}B NMR spectroscopy (Figure 9). In contrast to the result observed with **5**/MAOa (Figure 6), where there is no change in the spectrum over the reaction period, **5**/MAOb shows the appearance of a signal at 42 ppm. This same signal is observed in the combination of **4**/MAOb (Figure 10) suggesting that B/Al exchange is faster with the structure and composition of MAOb.

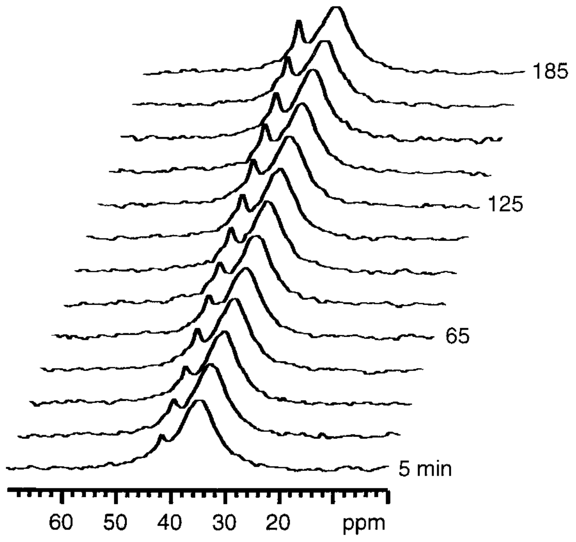

Figure 9. ^{11}B NMR of **5**/MAOb (Albemarle) versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

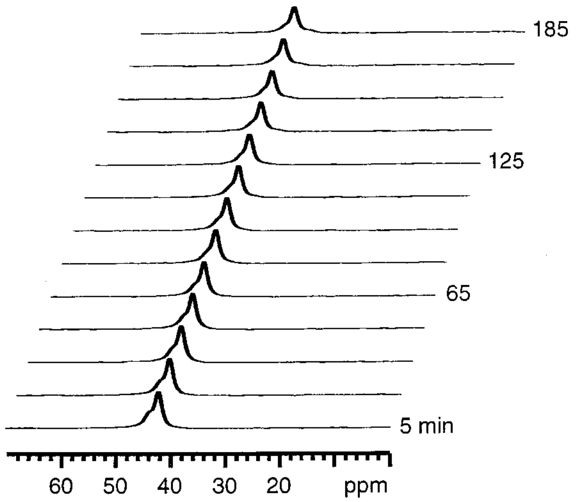

Figure 10. ^{11}B NMR of **4**/MAOb (Albemarle) versus time. Conditions: $[Zr] = 5 \times 10^{-4}$ M, Al:Zr = 500, 23 °C.

Summary

^{11}B NMR spectroscopy is a suitable method for monitoring the species produced by $(C_5H_5B\text{-}R)_2ZrCl_2$/MAO reaction mixtures. The observations presented indicate that alkoxy groups react with Al−Me functionalities in MAO or in the residual trimethylaluminum. Similarities in chemical shifts suggest that this transmetalation process results in the appearance of the catalyst derived from **4**/MAO. Smaller alkoxy groups, i.e. methoxy and ethoxy, exchange more slowly than their larger counterparts (cyclohexyloxy, benzyl, and *tert*-butoxy) and only under high aluminum concentrations.[28] Exchange reactions occur more readily with MAOb than with MAOa. The reason for the difference in rates is likely dependent on the aluminoxane structure and the ratio of residual trialkylaluminum.

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(28) A reviewer suggested the possibility that after coordination of the B−OR oxygen to aluminum, the *tert*-butyl group eliminates to form isobutylene, perhaps methane, and a $B-O-AlR_2$ complex, which undergoes further reaction to give B−Me. Similar kinds of processes can be envisioned for R = cyclohexyl, benzyl. However, with R = Et, Me, one would expect much slower rates (none for Me).

The ^{11}B NMR data, ethylene oligomerization reactions, and 1-decene reactions suggest that alkoxyboratabenzene catalysts are highly selective toward 1-alkene formation. Loss in selectivity observed for the catalysts **2**/MAO, **3**/MAO, and **6**/MAO is due to the formation of methylboratabenzene species, which react with the 1-alkenes.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques.[29] **1**,[6] **2**,[9] **3**,[9] **4**,[8] and C_5H_5B-PMe_3 [30] were prepared according to literature methods. Toluene, THF, pentane, and Et_2O were distilled from sodium benzophenone ketyl. 1-Decene was dried over 3 Å molecular sieves, degassed, and filtered through Celite. MAOa in toluene was purchased from Akzo Nobel Chemicals, Inc., and used as received. MAOb in toluene was obtained from Albemarle Corp. and used as received. Trimethylaluminum was purchased from Aldrich and used as received. NMR spectra were obtained using a Varian Unity 400 or 500 spectrometer. $^{11}B\{^1H\}$ (160 MHz) spectra were recorded at room temperature in a 10 mm quartz NMR tube and are referenced externally to $BF_3\cdot Et_2O$. Toluene was used as the solvent, and the spectra were recorded without locking or shimming the instrument, as this had a negligible effect on the line shape. The acquisition time used was 0.020 s with a 0.100 s delay and a spectral window of 60 015 Hz, collecting 2432 points per transient. The number of transients per FID collected was 3720. Spectra were recorded for 8 min every 15 min (preacquisition delay of 7 min), collecting 13 FIDs over the course of 3 h. Line broadening was set to 100 for Fourier transformations to obtain reasonable signal to noise without significant changes in line shape. Preparation of the samples is described below. ^{1}H and ^{13}C NMR spectra were referenced internally to solvent resonances and are reported downfield from $SiMe_4$. Elemental analyses were performed by Desert Analytics, Inc., Tucson, AZ.

Na(C_5H_5B-OMe). NaOMe (202 mg, 3.74 mmol) and C_5H_5B-PMe_3 (567 mg, 3.73 mmol) were combined in 15 mL of THF and stirred for 4 days at room temperature. Removal of volatiles in vacuo afforded an off-white solid (468 mg, 3.60 mmol, 97%). ^{1}H NMR (THF-d_8, 400 MHz): δ 3.47 (s, 3H, BOCH_3), 5.67 (d, 2H, CHCHCHB, $^3J_{HH}$ = 10.1 Hz), 5.72 (t, 1H, CHCHCHB, $^3J_{HH}$ = 6.9 Hz), 7.16 (dd, 2H, CHCHCHB, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 10.5 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 100 MHz): δ 52.7 (BOCH$_3$), 104.8 (CHCHCHB), 110.6 (br, CHCHCHB), 135.6 (CHCHCHB). $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz): δ 38 (s, br).

K(C_5H_5B-O^{t}Bu). KO^{t}Bu (181 mg, 1.61 mmol) and $C_5H_5B\cdot PMe_3$ (245 mg, 1.61 mmol) were placed in a 100 mL flask with a magnetic stir bar and 10 mL of THF. This was heated to 70 °C overnight under argon, resulting in an off-white precipitate. Removal of volatiles in vacuo afforded an off-white solid (288 mg, 1.53 mmol, 95%). ^{1}H NMR (THF-d_8, 400 MHz): δ 1.34 (s, 9H, BOC(CH_3)$_3$), 5.57 (tt, 1H, CHCHCHB, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 6.8 Hz), 5.65 (dd, 2H, CHCHCHB, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 10.7 Hz), 7.02 (dd, 2H, CHCHCHB, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 100 MHz): δ 31.5 (BOC(CH$_3$)$_3$), 104.2 (CHCHCHB), 135.8 (CHCHCHB). Low solubility in THF precludes observation of BOC(CH$_3$)$_3$ and CHCHCHB peaks. $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz): δ 39 (s, br).

(C_5H_5B-OMe)$_2$ZrCl$_2$ (5). Na(C_5H_5B-OMe) (439 mg, 3.38 mmol) and $ZrCl_4(THF)_2$ (634 mg, 1.68 mmol) were placed in a 100 mL flask with a magnetic stir bar. Et_2O (ca. 30 mL) was condensed on the solids at −78 °C. This mixture was stirred and slowly warmed to room temperature overnight, giving a bright yellow slurry. Volatiles were removed in vacuo, and the product was extracted with toluene. Filtration through Celite and removal of solvent under vacuum afforded a crystalline golden yellow solid (435 mg, 1.16 mmol, 69%). ^{1}H NMR (C_6D_6, 400 MHz): δ 3.57 (s, 6H, BOCH_3), 5.61 (dd, 4H, CHCHCHB, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 11.0 Hz), 5.89 (tt, 2H, CHCHCHB, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 6.9 Hz), 7.21 (dd, 4H, CHCHCHB, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 11.0 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 52.9 (BOCH$_3$), 104.5 (CHCHCHB), 116.5 (br, CHCHCHB), 147.5 (CHCHCHB). $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz): δ 36 (s, br). Anal. Calcd for $C_{12}H_{16}B_2Cl_2O_2Zr$: C, 38.33; H, 4.29. Found: C, 36.52; H, 3.70.

(C_5H_5B-O^{t}Bu)$_2$ZrCl$_2$ (6). K(C_5H_5B-O^{t}Bu) (103 mg, 0.548 mmol) and $ZrCl_4(THF)_2$ (104 mg, 0.274 mmol) were placed in a 100 mL flask with a magnetic stir bar. THF (15 mL) was condensed on the solids at −78 °C. This mixture was stirred and slowly warmed to room temperature for 18 h, giving a hazy yellow mixture. Volatiles were removed in vacuo, and the product was extracted with Et_2O. Filtration through Celite and removal of solvent under vacuum afforded a yellow semisolid. This was crystallized from pentane to give yellow microcrystals of **6** (79 mg, 0.17 mmol, 63%). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.35 (s, 18H, BOC(CH_3)$_3$), 5.70 (dd, 4H, CHCHCHB, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 11.1 Hz), 5.91 (tt, 2H, CHCHCHB, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 6.7 Hz), 7.27 (dd, 4H, CHCHCHB, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 11.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 31.3 (BOCH$_3$), 74.5 (BOC(CH$_3$)$_3$), 103.5 (CHCHCHB), 118.5 (br, CHCHCHB), 146.9 (CHCHCHB). $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz): δ 36 (s, br). Anal. Calcd for $C_{18}H_{28}B_2Cl_2O_2Zr$: C, 46.98; H, 6.13. Found: C, 46.70; H, 5.85.

^{11}B NMR of (C_5H_5B-R)$_2$ZrCl$_2$/MAO Mixtures. In the glovebox, a stock solution (10.0 μmol of Zr/g of solution) of the precatalyst was prepared. Into separate 5 mL vials was weighed 180 mg (1.80 μmol of Zr) of stock solution, 235 mg of MAO (10.3% Al by weight, 897 μmol of Al), and 2.24 g of toluene. For experiments with Albemarle MAO, 178 mg (13.42% Al by weight, 901 μmol) was used. The (C_5H_5B-R)$_2$ZrCl$_2$ solution was then added to the MAO and the mixture transferred to a 10 mm quartz NMR tube using the preweighed toluene to rinse in the residual reagents left in the vials. The $^{11}B\{^1H\}$ spectra were then acquired immediately as described in the general remarks.

Concentrated Reactions. In the glovebox, a stock solution (50.0 μmol of Zr/g of solution) of the appropriate (C_5H_5B-R)$_2$ZrCl$_2$ was prepared. Into separate 5 mL vials was weighed 180 mg (9.00 μmol of Zr) of stock solution, 1.18 g of MAO (10.3% Al by weight, 4.50 mmol), and 0.78 g of toluene. The (C_5H_5B-R)$_2$ZrCl$_2$ solution was then added to the MAO suspension and the mixture transferred to a 10 mm quartz NMR tube using the preweighed toluene to rinse in the residual reagents left in the vials. The $^{11}B\{^1H\}$ spectra were then acquired immediately, as described in the general remarks.

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 μmol/g of toluene solution. A 1.00 g fraction of this solution was combined with the appropriate amount of MAO (1000:1 Al:Zr based on overall aluminum). Immediately after addition a color change to a deeper yellow or orange is typically 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 5 s, and the flask was brought to 60 °C. After 30 min of exposure to 1 atm of ethylene, the assembly was reweighed to the nearest 0.01 g for activity measurements. The reaction was quenched using ∼3 mL of water, and the

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(29) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

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

resulting aluminum-containing salts were dissolved in aqueous base. The toluene layer was extracted and analyzed using ^{1}H NMR spectroscopy, GC, and GC-MS.

1-Decene Isomerization. A 15 μmol amount of the precatalyst was combined with 500 equiv of aluminum as 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 immediately quenched with water. The mixtures were then diluted with 1 mL of cyclohexane, dried with anhydrous $MgSO_4$, and filtered.

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