Ethoxyboratabenzene Zirconium Complexes: Catalysts for α-Olefin Production

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Well-defined electrophilic organometallic catalysts are conspicuously absent in ethylene oligomerization technology.[1] This is somewhat surprising in view of classical formulations containing aluminum alkyls and group 4 halides, or alkoxides, available for this purpose.[2] Metallocene catalysts could play an important role in improving the production of 1-alkenes (known in industry as α-olefins), especially when their extremely fast rates of ethylene insertion are considered. Their current drawback is that metallocene catalysts with high propensity for ethylene generally display slow rates of β-hydrogen elimination.[3] As a result, polymers form even under low monomer pressure.

Recent reports show that boratabenzene ligands[4] are suitable substitutes for cyclopentadienyl (Cp) ligands and enable tuning of the electron density and the reactivity of electrophilic metals. The exocyclic substituent on boron plays an important role in this respect. Amine substituents allow for strong B−N π orbital overlap and weaken the metal−boron interaction.[5] In $[C_5H_5B-N(i-Pr)_2]_2ZrCl_2$ (**1**), the Zr−B distance (2.98(1) Å) is too long for effective bonding. Weaker donors, such as phenyl, cannot compensate effectively for the electronic requirements of boron and shorter Zr−B distances are observed.[6] The average Zr−B distance observed for $[4-tert-C_4H_9-C_5H_4B-Ph]_2ZrCl_2$ (**2**) is significantly shorter (2.80(3) Å) than that of **1**.[7] Activation of **1** and $[C_5H_5B-Ph]_2ZrCl_2$ (**3**) with methylaluminoxane (MAO) leads to catalysts with different reactivities. Addition of 1 atm of C_2H_4 to **1**/MAO results in formation of polyethylene, whereas **2**/MAO under similar reaction conditions forms 2-alkyl-1-alkenes as the major product (>90%).[7]

In this paper we report on the synthesis and reactivity of the ethoxyboratabenzene complex $[C_5H_5B-OEt]_2ZrCl_2$ (**4**). Compound **4** serves as a precatalyst for the selective formation of 1-alkenes from C_2H_4. This reaction demonstrates the powerful concept of selectivity control by choice of the exocyclic boron substituent in boratabenzene-based catalysts.

Sodium ethoxyboratabenzene can be prepared by modification of the Ashe protocol[8] or by the more recent procedure of Fu.[9]

Figure 1. ORTEP view of **4**, showing the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Zr−B, 2.826(2); Zr−C(1), 2.661(3); Zr−C(2), 2.585(3); Zr−C(3), 2.497(3); Zr−C(4), 2.580(3); Zr−C(5), 2.652(3).

Reaction of 2 equiv of $Na[C_5H_5B-OEt]$ with $ZrCl_4$ in Et_2O gives **4** in 71% yield (eq 1).
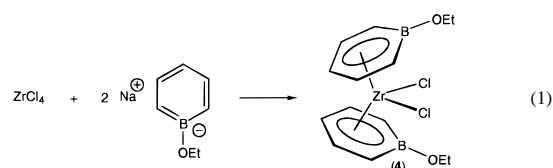
A single-crystal X-ray diffraction study of **4** revealed the molecular structure shown in Figure 1. The overall geometry resembles a group 4 bent metallocene and does not deviate significantly from the structures of **1** and **2**. There are some important subtle details. The Zr−B distance (2.83(1) Å) in **4** is virtually identical to the average Zr−B distance in **2** and is shorter than that in **1**. Insofar as these parameters can be used as a measure of Zr−B orbital overlap, they suggest that the electronic density at Zr should be similar in **2** and **4** but it is expected to be somewhat higher for **1**. The oxygen atoms in **4** are sp^2 hybridized ($\angle B-O-C = 119.7(2)°$) and the short B−O distance[10] (1.372(4) Å) suggests π overlap between the two atoms. We note that in this static structure all boratabenzene protons are inequivalent. In solution, by ^1H and ^{13}C NMR spectroscopies, the symmetric structure is observed instead. Only three resonances are observed for the boratabenzene protons (δ 7.22, 5.88, 5.57 in toluene-d_8) even at temperatures as low as 192 K. Therefore, rotation about the B−O bond is fast relative to the NMR time scale, which suggests a low activation barrier and a weak B−O π bond.[11]

Ethylene is consumed quickly by solutions of **4**/MAO. GC/MS analysis (Figure 2a) of a reaction run under 1 atm of C_2H_4, $[4] = 1.2 \times 10^{-4}$ M, $[Al]/[Zr] = 500$, and 60 °C for 30 min shows that the product is a distribution of 1-alkenes of varying chain lengths.[12] Each peak in Figure 2a differs in mass by 28 au, corresponding to an inserted ethylene molecule. There is no evidence of odd-carbon alkenes or alkanes of any type, indicating no chain transfer to aluminum. Figure 2b shows the

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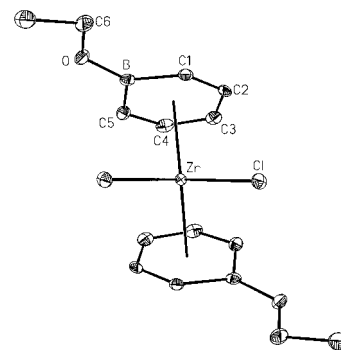(7) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492.

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(11) For comparison, note that the barrier to B−N rotation in **1** is $\Delta G^{\ddagger} = 18.2 \pm 0.5$ kcal/mol at 62 °C. See ref 7.

(12) Lower temperatures (0 °C) lead to higher molecular weight material. DSC analysis of the precipitate from these reactions is consistent with polyethylene.

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Table 1

precatalyst	Al/Zr	time (min)	temp (°C)	mole percentage[a]			activity[b]	average inserted ethylene units
				1-alkene	2-alkyl-1-alkene	2-alkene		
4	500	30	60	100	0	0	160	6.5
4	500	60	60	100	0	0	130	7
4	1000	30	60	94.8	4.6	0.6	325	8
4	1000	60	60	88.8	6.9	4.3	240	7
4	1000	30	0				240	polymer (T_m = 131 °C)[c]
3	500	30	60	71.5	20.6	7.9	675	6.5
3	1000	30	60	45.7	41.6	12.7	920	7
3	1000	60	60	42.4	44.4	13.2	700	7
3	1000	30	0				735	polymer (T_m = 124 °C)[c]
Cp_2ZrCl_2	1000	30	0				450	polymer (T_m = 134 °C)[c]

[a] Determined by ^1H NMR spectroscopy. [b] Activity is in kilograms of ethylene consumed per mole of catalyst per hour; $[Zr] = 1.2 \times 10^{-4}$ M. [c] Melting points determined by DSC.
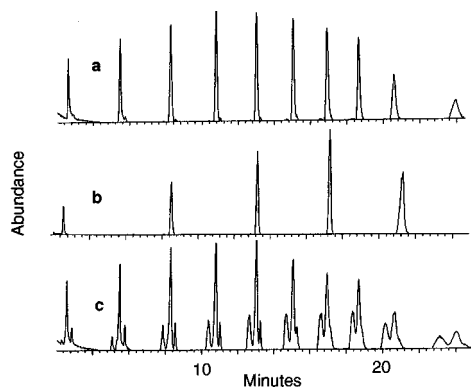

Figure 2. Partial GC/MS trace of (a) the product from the reaction of **4**/MAO and 1 atm of C_2H_4; (b) an equimolar mixture of 1-decene, 1-tetradecene, 1-octadecene, docosane, and hexacosane; (c) the product from the reaction of **3**/MAO and 1 atm of C_2H_4.

GC/MS trace corresponding to an equimolar mixture of 1-decene, 1-tetradecene, 1-octadecene, docosane, and hexacosane for comparison.[13] ^1H NMR spectroscopy provides supporting information. Only terminal olefins (δ 4.91, 4.98, and 5.75) are observed, and the integration of these resonances relative to the methylene and methyl peaks (δ 1.28 and 0.90) determines that the average number of inserted ethylene units is approximately 6 or 7.
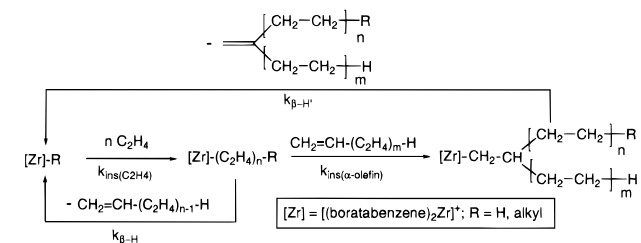
The effect of reaction conditions on the product distribution is shown in Table 1. Activity measurements are accurate to ±5% on multiple runs. The best selectivities are observed for lower [Al]/[Zr] ratios, albeit with lower overall activity. There is also a drop in activity by **4**/MAO over time.[14] The product distribution obtained using **3**/MAO is shown in Figure 2c and Table 1.[15] These data, coupled with NMR analysis, show that **3**/MAO is less selective, producing 1-alkenes, 2-alkenes, and 2-alkyl-1-alkenes in various ratios. Overall, **4**/MAO is approximately three times less active toward C_2H_4 than **3**/MAO and one half as reactive as Cp_2ZrCl_2/MAO under similar reaction conditions.

Activated forms of **3** and **4** therefore give different products when reacted with 1 atm of ethylene. The relationship between

Scheme 1

selectivity and the relative rates of the catalytic cycles leading to 1-alkenes and 2-alkyl-1-alkenes is better understood by noting the different possible outcomes shown in Scheme 1. The amount of product indicates that $k^3_{ins(C2H4)}$ is approximately three times larger than $k^4_{ins(C2H4)}$ (here, we assume that the concentration of ethylene and the number of activated metal species are similar for both reactions). Similarly, since the average number of inserted monomers is similar in both cases, $k^3_{\beta-H}$ is three times larger than $k^4_{\beta-H}$. The two catalysts differ more greatly on the rates of subsequent reactions. Formation of 2-alkyl-1-alkenes is negligible for **4**, and therefore, $k^3_{ins(\alpha-olefin)}$ is larger than $k^4_{ins(\alpha-olefin)}$.[16] For the aminoboratabenzene catalyst derived from **1** and MAO, the value of $k^1_{ins(C2H4)}[C_2H_4]$ under 1 atm of monomer is much larger than $k^1_{\beta-H}$, thus resulting in polymer formation.

In summary, we have shown that **4**/MAO serves to prepare 1-alkenes from ethylene. This selectivity expands the scope of metallocene-like catalysts into new manufacturing methods for industrially important molecules. We have also shown further evidence that the reactivity of boratabenzene catalysts can be directed by carefully choosing the boron substituent. We believe that differences in the electronic density at the metal site are important in this respect, since the steric properties of phenylboratabenzene and ethoxyboratabenzene are similar. Overall, these results suggest that reactions mediated by Cp-containing catalysts could be altered significantly by exchanging Cp for different boratabenzene ligands within the ligand sphere of the catalyst.[7,17] Current studies are aimed at applications of this concept.

(13) The higher molecular weight alkanes show essentially the same retention time as 1-alkenes of similar molecular weight. The area of the peaks are proportional to the total ion count, with heavier hydrocarbons yielding higher trace abundances.

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(15) These reaction conditions are more dilute than those used in ref 7 and discourage the formation of 2-alkyl-1-alkenes.

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