

(Phenylboratabenzene)zirconium Complexes: Tuning the Reactivity of an Olefin Polymerization Catalyst

Guillermo C. Bazan* and George Rodriguez

Department of Chemistry, University of Rochester, Rochester, New York 14627-0216

Arthur J. Ashe III,* Saleem Al-Ahmad, and Jeff W. Kampf

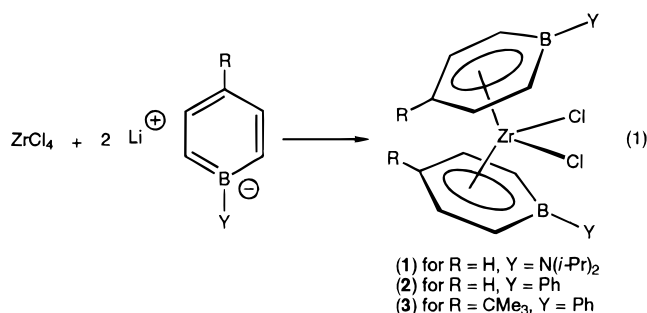
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

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Summary: The reaction of 2 equiv of lithium 1-phenylboratabenzene with $ZrCl_4$ in ether affords bis(1-phenylboratabenzene)zirconium dichloride (**2**), while [4-*tert*- $C_4H_9C_5H_4BPh$] $_2ZrCl_2$ (**3**), obtained in a similar manner, was subjected to a single-crystal X-ray diffraction study. The reaction of a solution of **2** and methylaluminoxane (MAO) with C_2H_4 (1 atm, 25 °C) affords ethylene oligomers (dimers of 1-alkenes as the major product, together with minor amounts of 1- and 2-alkenes).

The development of new metallocene-based homogeneous catalysts for olefin polymerization is of immense practical importance¹ and continues to attract intense research.² Bis(boratabenzene)metal complexes,³ e.g., **1–3**, result from the replacement of the metallocene cyclopentadienyl groups by the aromatic heterocycle boratabenzene.⁴ Recently, catalysts prepared from [C₅H₅BN(*i*-Pr)₂] $_2ZrCl_2$ (**1**) have been found to have high activity.⁵ Since the boron atoms of **1** interact strongly with their exocyclic substituents, we have proposed that boratabenzene–metal catalysts may be electronically tunable by changing the pendant group. In this communication, we report on the synthesis and characterization of bis(1-phenylboratabenzene)zirconium dichlorides (**2** and **3**) and show that olefin polymerization by **2** involves increased rates of β -hydrogen elimination.

The reaction of $ZrCl_4$ with 2 equiv of Li[C₅H₅BPh]⁶ in ether produces [C₅H₅BPh] $_2ZrCl_2$ (**2**) in 80% yield (eq 1).⁷ Crystals suitable for X-ray diffraction could only be obtained for the derivative [4-*tert*-C₄H₉C₅H₄BPh] $_2ZrCl_2$ ⁸ (**3**), for which the molecular structure is illustrated in Figure 1.⁹ The sterically demanding *tert*-butyl groups of **3** are positioned to the sides of the open metallocene wedge, which brings the less sterically demanding B–Ph groups near the more crowded closed face of the wedge. The Zr atom is η^6 -coordinated to both rings and



is approximately equidistant from each of the 10 ring carbon atoms (average Zr–C_α = 2.62(3) Å, average Zr–

(7) Bis(1-phenylboratabenzene)zirconium dichloride (**2**). A solution of LDA (6.5 mmol) in 10 mL of ether was added dropwise to a solution of 1-phenyl-1-boracyclohexa-2,5-diene (1.0 g, 6.5 mmol) in 20 mL of ether at –78 °C. The color changed to yellow when the reaction mixture was allowed to warm to room temperature. After this solution was recooled to –78 °C, it was added with stirring to a suspension of $ZrCl_4$ (0.75 g, 3.25 mmol) in 10 mL of ether at –78 °C. The reaction mixture was allowed to warm to room temperature with stirring over 4 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene. After filtration, the filtrate was concentrated under reduced pressure and treated with pentane. Upon standing in the freezer for 24 h, a yellow crystalline product was obtained. The product was collected by filtration, washed with pentane, and dried in vacuum affording 1.30 g (80%) of product, mp 165 °C. HRMS(EI): calcd for C₂₂H₂₀¹¹B₂³⁵Cl₂⁹⁰Zr *m/e*, 466.0175; found *m/e*, 466.0164. ¹H NMR (C₆D₆): δ 6.17 (t, *J* = 6.5 Hz, H(4)), 6.57 (d, *J* = 11.2 Hz, H(2,6)), 7.22 (dd, *J* = 11.2, 6.8 Hz, H(3,5)), 7.32 (t, *J* = 7.2 Hz, *p*-Ph), 7.41 (t, *J* = 7.2 Hz, *m*-Ph), 7.94 (d, *J* = 7.2 Hz, *o*-Ph). ¹³C NMR (C₆D₆): δ 112.7 (C(4)), 126.4 (C(2,6)), 146.8 (C(3,5)), 128.9 (*m*-Ph), 130.7 (*p*-Ph), 133.9 (*o*-Ph), *ipso*-Ph not observed. ¹¹B NMR (C₆D₆): δ 39.6. Anal. Calcd for C₂₂H₂₀B₂Cl₂Zr: C, 56.40; H, 4.31. Found: C, 56.31; H, 4.24.

(8) Bis(4-*tert*-butyl-1-phenylboratabenzene)zirconium dichloride (**3**): A solution of 4-*tert*-butyl-1,1-dibutyl-1-stannacyclohexa-2,5-diene (2.0 g, 5.6 mmol) in 10 mL of pentane was added with stirring to a solution of phenylboron dichloride (0.94 g, 5.9 mmol) in 20 mL of pentane at –78 °C. The reaction mixture was allowed to stir at –78 °C for 1 h and then allowed to warm to room temperature. The solvent and dibutyltin dichloride were removed by vacuum distillation, leaving a residue of 0.5 g (43%) of 4-*tert*-butyl-1-phenyl-1-boracyclohexa-2,5-diene. ¹H NMR (C₆D₆): δ 0.85 (s, 9H, CMe₃), 2.67 (m, 1H, CH(4)), 7.36 (m, 7H), 8.21 (m, 2H, *o*-Ph). This crude product was used without further purification. A solution of LDA (2.3 mmol) in 10 mL of ether was added dropwise to a solution of 4-*tert*-butyl-1-phenyl-1-boracyclohexa-2,5-diene (0.5 g, 2.3 mmol) in 20 mL of ether at –78 °C. The color changed to yellow on warming to room temperature. After this solution was recooled to –78 °C, it was added dropwise with stirring to a suspension of $ZrCl_4$ (0.28 g, 1.2 mmol) in 10 mL of ether at –78 °C. The reaction mixture was allowed to warm to room temperature with stirring over 4 h. The solvent was removed under reduced pressure, leaving a yellow residue which was extracted with hexane (4 × 20 mL). The hexane extracts were cooled in the freezer for 12 h, which afforded 0.25 g (36%) of yellow crystals, mp 118–120 °C. HRMS(EI): calcd for C₃₀H₃₆¹¹B₂³⁵Cl₂⁹⁰Zr *m/e*, 578.1427; found *m/e*, 578.1438. ¹H NMR (C₆D₆): δ 1.19 (s, CMe₃), 6.94 (d, *J* = 11.4 Hz, H(2,6)), 7.47 (d, *J* = 11.4 Hz, H(3,5)), 7.35 (t, *J* = 7.4 Hz, *p*-Ph), 7.48 (t, *J* = 7.4 Hz, *m*-Ph), 8.19 (d, *J* = 7.4 Hz, *o*-Ph). ¹³C NMR (C₆D₆): δ 31.4 (CMe₃), 37.0 (CMe₃), 127.7 (C(2,6)), 137.6 (C(4)), 143.9 (C(3,5)), 128.9 (*m*-Ph), 130.9 (*p*-Ph), 133.7 (*o*-Ph), *ipso*-Ph not observed. ¹¹B NMR (C₆D₆): δ 36.9. Anal. Calcd for C₃₀H₃₆B₂ZrCl₂: C, 62.08; H, 6.26. Found: C, 62.33; H, 6.29. For the synthesis of 1,1-dibutyl-4-*tert*-butyl-1-stannacyclohexa-2,5-diene, see: ref 6 and Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

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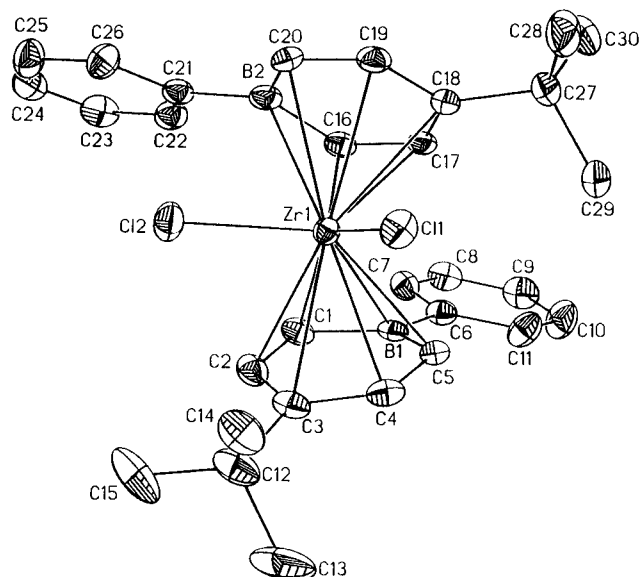


Figure 1. ORTEP view of **3**, showing the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Zr–B(1), 2.826(2); Zr–B(2), 2.773(3); Zr–C(1), 2.619(2); Zr–C(2), 2.608(2); Zr–C(3), 2.660(2); Zr–C(4), 2.599(2); Zr–C(5), 2.606(2); Zr–C(16), 2.577(2); Zr–C(17), 2.584(2); Zr–C(18), 2.668(2); Zr–C(19), 2.659(2); Zr–C(20), 2.663(2).

$C_{\beta} = 2.61(2)$ Å, average Zr– $C_{\gamma} = 2.66(1)$ Å, while the Zr–B distance (ave 2.80(3) Å) is somewhat longer.¹⁰ The geometry of the ligand and its juxtaposition to the metal are virtually identical to those found in late transition metal complexes,^{3b,11} implying an invariant electronic character for phenylboratabenzene. Since phenylboratabenzene is a poorer donor than Cp,^{3b,c} the Zr atoms of **2** and **3** should be more electrophilic than those of standard metallocenes. In marked contrast, the Zr atom of **1** shows a large slip-distortion away from B (Zr–B = 2.98 Å) and toward C_{γ} (Zr– $C_{\gamma} = 2.483(5)$ Å).⁵ The strong π donation to B by the pendant N(*i*-Pr)₂ group of **1** saturates the electropositive boron, making the Zr of **1** less electrophilic than that of **2**.

In the presence of MAO, **1** produces high molecular weight polyethylene under 1 atm of C₂H₄. The analogous reaction with **2** proceeds differently.¹² At pressures under 2 atm, the major product is a mixture of 2-alkyl-1-alkenes of various chain lengths. Figure 2 shows part of the GC/MS trace for the product obtained after 30

(9) Crystal data for C₃₀H₃₆B₂Cl₂Zr: space group *P*2₁/*c* with *a* = 10.0660(8) Å, *b* = 12.2679(10) Å, *c* = 22.807(2) Å, $\beta = 91.472(5)^{\circ}$, *Z* = 4, $\rho = 1.369$ g/cm³. A total of 7454 reflections (h,k,l) were collected in the range $2.62^{\circ} < 2\theta < 26.00^{\circ}$, with 5519 being used in the structure refinement by full-matrix least-squares techniques (462 variables). Final R1 = 0.0294, wR2 = 0.0596.

(10) The steric effects of the ring substituents on the hapticity of the boratabenzene ligands of **3** are probably minor since the electronically similar but sterically divergent 1-methylboratabenzene is η^6 -coordinated in (C₅H₅BMe)₂ZrCl₂. Herberich, G. E. *Pure Appl. Chem.*, in press.

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(12) A typical procedure follows. A 2 mL toluene solution of **2** (10 mg, 0.021 mmol) was added dropwise to a 20 mL toluene solution of MAO (0.600 g, 10.3 mmol). After the reaction mixture was stirred for 10 min, the reaction vessel was evacuated and 1 atm of ethylene introduced with vigorous stirring. After 40 min, the reaction was quenched with 30 mL of a 10% solution of HCl in methanol. The organic layer was separated from the aqueous fraction and placed under vacuum to remove the solvent. This fraction gave 1.199 g of an oily organic material. The product was characterized by GC/MS and ¹H and ¹³C NMR as a mixture of 2-alkyl-1-alkenes (~80%), 1-alkenes (~10%), and 2-alkenes (~10%).

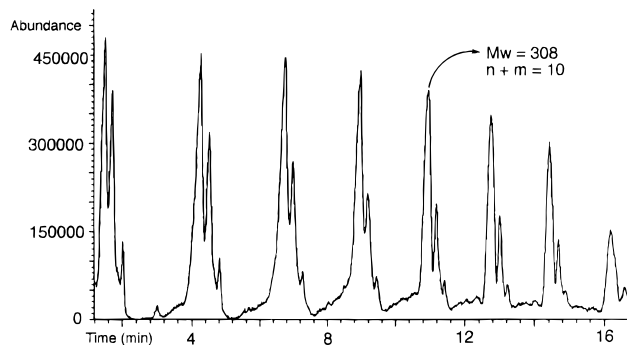


Figure 2. Partial GC/MS trace of the product mixture obtained from reaction of **2**/MAO and 1 atm of C₂H₄.

min (*T* = 25 °C, 1 atm of C₂H₄). Each peak differs in mass by one C₂H₄ unit while their “fine structure” is due to different isomers (*i.e.*, different *m* + *n* combinations). Also produced at 1 atm of C₂H₄ are 1-alkenes and 2-alkenes in 11% and 9% yields, respectively, as determined by NMR spectroscopy.¹³ The **2**/MAO catalyst mixture forms polyethylene at higher temperatures, and there is a nearly linear dependence of *M_w* (*M_w* = weight average molecular weight) on ethylene pressure (at 60 °C: *M_w* = 10K (30 psi); *M_w* = 20K (75 psi); *M_w* = 110K (300 psi)). Monomer consumption increases with pressure and temperature (*i.e.*, a rate of 1180 kg of PE/(h [Zr] mol) is observed at 60 °C and 300 psi).

In analogy to well-established metallocene chemistry,² we propose that, at low ethylene pressure, **2**/MAO/C₂H₄ react according to Scheme 1. Multiple C₂H₄ insertions into hydride **A**¹⁴ result in the propagating alkyl **B**. Fast β -H elimination from **B** limits chain growth generating 1-alkenes and **A**. At longer reaction times, the concentration of 1-alkenes increases and their insertion into **B** takes place to give the β -disubstituted alkyl **C**. The 2-alkyl-1-alkenes (**D**) arise from β -H elimination at **C**, which also regenerates **A**. The 2-alkenes are probably the result of 2,1-insertion, followed by β -hydrogen elimination.¹⁵

For a given unit of reaction time, the total mass of organic product reflects the rate of C₂H₄ uptake. At 1 atm and [MAO]/[**2**] = 480, the activity obtained is 84 Kg of 2-alkyl-1-alkenes/(h [Zr] mol). For **1**, under similar conditions ([MAO]/[**1**] = 450), one obtains 69 kg of PE/(h [Zr] mol). Therefore, under the experimental conditions described above, changing the boron substituent from diisopropylamine to phenyl increases the rate of β -H elimination from **B** more greatly (*k_β* in Scheme 1) than the rate of ethylene insertion into **A** (*k_{ins}*).

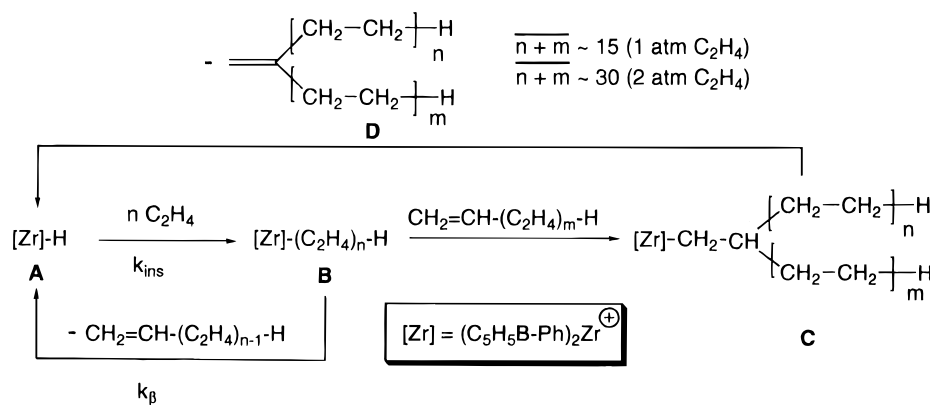
The following observations are consistent with Scheme 1. Quenching after 5 min at 1 atm of C₂H₄ gives a product of 60% 1-alkenes with 40% 2-alkyl-1-alkenes. At 15 min, the olefin ratio changes to 29% 1-alkenes to 71% 2-alkyl-1-alkenes. Doubling the ethylene pressure

(13) ¹H NMR (CDCl₃, 300 MHz): δ 4.58 (s, 2-alkyl-1-alkenes, 2H), 4.81 (dm, *J* = 10.5 Hz, 1-alkenes, 1H), 4.89 (dm, *J* = 17 Hz, 1-alkenes, 1H), 5.3 (m, 2-alkenes, 2H), 5.7 (m, 1-alkenes, 1H). ¹³C NMR (75.3 MHz, CDCl₃): δ 107.5 (2-alkyl-1-alkenes), 108.6 (2-alkyl-1-alkenes), 114.3 (1-alkenes), 123.7 (2-alkenes), 131.1 (2-alkenes), 139.3 (1-alkenes), 150.5 (2-alkyl-1-alkenes), 151.9 (2-alkyl-1-alkenes).

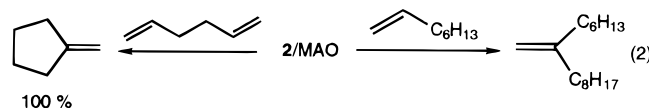
(14) We assume that MAO serves its standard role; alkylation followed by ligand extraction. The hydride is generated from insertion of C₂H₄ followed by β -hydrogen elimination.

(15) For a discussion of the regiochemistry of 1-alkene insertion in Ziegler–Natta catalysts see: Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538.

Scheme 1



from 1 to 2 atm increases the $(m + n)$ average from 15(1) to 30(1). Direct addition of 1-alkenes yields the expected products. For example, 1-octene is dimerized to 2-hexyl-1-decene by **2**/MAO in less than 5 min (eq 2).¹⁶ In addition, the reaction of 1,5-hexadiene with



2/MAO results in quantitative production of methylenecyclopentane (eq 2).

In summary, we have shown that a change of the boron substituent of a boratabenzene-zirconium catalyst has a profound effect on its chemical reactions. While ((diisopropylamino)boratabenzene)zirconium catalysts form high molecular weight polyethylene at low monomer pressure, the more electrophilic (phenyl-

boratabenzene)zirconium catalysts increase the rate of β -hydrogen eliminations so that 1-alkenes and their dimers are obtained. In the broader context, we have demonstrated that boratabenzenes are electronically tunable surrogates for cyclopentadienyl in an important class of organometallic compounds. Since the cyclopentadienyl ligand is ubiquitous in organometallic chemistry, it should be possible to effect similar modification of other important reactions.¹⁷

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and ORTEP diagram for **3** (9 pages). Ordering information is given on any current masthead page.

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(16) Dimerization of 1-octene: To a 10 mL toluene solution of **2** (10 mg, 0.21 mmol) and MAO (600 mg, 0.01 mol) was added 1-octene (0.5 g, 4.5 mmol). The reaction was quenched after 2 h with 20 mL of a 10% solution of HCl in methanol. The organic layer was separated and the solvent removed to give 453 mg of a clear colorless liquid. ¹H NMR (CDCl₃, 400 MHz): δ 4.85 (s, 2H, H₂C=C), 2.05 (m, 4H, H₂C=C(CH₂)₂), 1.45 (m, 4H, CH₂CH₃), 1.32 (b, 16H, CH₂), 0.91 (m, 6H, CH₃). ¹³C NMR (CDCl₃): δ 150.1, 109.1, 36.5, 32.3, 32.1, 30.6, 30.2, 29.9, 29.5, 28.2, 28.1, 23.05, 23.03, 14.3 (two carbon resonances overlap). GC/MS shows a single component with MW = 224. A similar procedure was carried out for the cyclization of 1,5-hexadiene to methylenecyclopentane.

(17) For an earlier perceptive example, see: Bönemann, H. *Angew. Chem., Int. Ed., Engl.* **1985**, *24*, 248.