Bridged Boratabenzene Zirconium Complexes: Analogues of the *ansa*-Zirconocene Polymerization Catalysts

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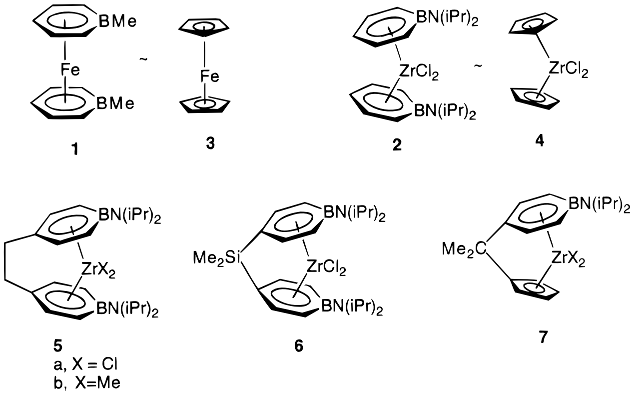
Ethylene-bridged bis(*N*,*N*-diisopropyl-1-aminoboratabenzene-4-yl)zirconium dichloride (**5a**), dimethylsilyl-bridged bis(*N*,*N*-diisopropyl-1-aminoboratabenzene-4-yl)zirconium dichloride (**7a**), and dimethylmethylene-bridged (cyclopentadienyl)(*N*,*N*-diisopropyl-1-aminoboratabenzene-4-yl)zirconium dichloride (**6a**) have been prepared. X-ray crystal structures of the dimethyl derivatives of **5** and **7** show that the complexes closely resemble the corresponding *ansa*-zirconocenes. When activated by excess methylaluminoxane, **5a**, **6a**, and **7a** are catalysts for the polymerization of olefins.

Introduction

Electrophilic metallocenes of the group 4 elements have uses as homogeneous catalysts for olefin polymerization.[1] Major attention has focused on the *ansa*-metallocenes in which the two cyclopentadienyl rings are connected by a short molecular bridge.[2,3] Although a number of bridging groups have been studied, the smaller bridges consisting of one carbon atom,[2b,4] two carbon atoms,[2] or one silicon atom[5] are most commonly used. Certain of these *ansa*-metallocenes have enhanced catalytic activity and are stereoselective. In part this derives from widening of the metallocene wedge and the greater rigidity of the constrained active site.[1]

Chart 1. Structures 1−7



Bis(boratabenzene) metal complexes,[6,7] e.g. **1**[8] and **2**,[9] are analogous to the corresponding metallocenes **3** and **4**. We recently reported that catalysts prepared from **2** and **4** have nearly identical activity toward polymerization of ethylene.[9,10] Thus an investigation of bridged boratabenzene metal complexes analogous to the *ansa*-metallocenes is desirable. We have now developed syntheses of bridged bis(boratabenzene) zirconium complexes **5** and **6**, which involve bridges of two carbon atoms and one silicon atom, respectively. We have also prepared a related mixed cyclopentadienyl−boratabenzene complex **7**, which has a one carbon atom bridge. Crystal structures of **5b** and **7b** demonstrate their considerable similarity to the corresponding *ansa*-metallocenes. (See Chart 1 for structures **1**−**7**.)

Syntheses

ansa-Metallocenes are usually prepared by first covalently linking the cyclopentadienyl ligands followed by their coordination to the metal.[3] We have adopted this synthetic strategy for bridged boratabenzene complexes. In principle bridging of the boratabenzene

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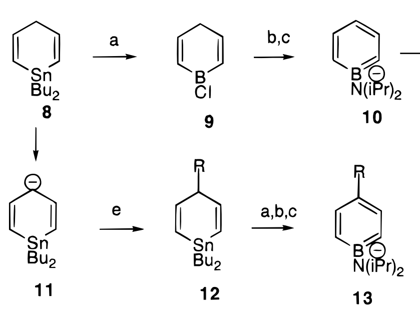
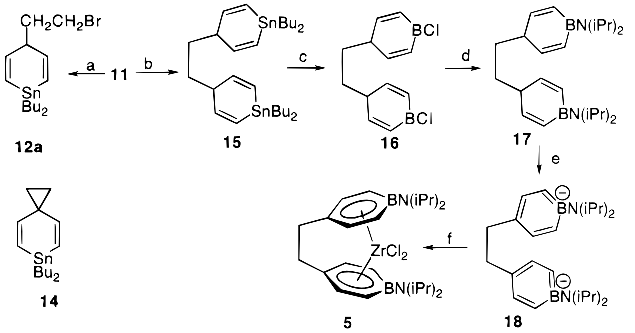
Scheme 1. Synthesis of 4-Substituted Boratabenzenes^{a}



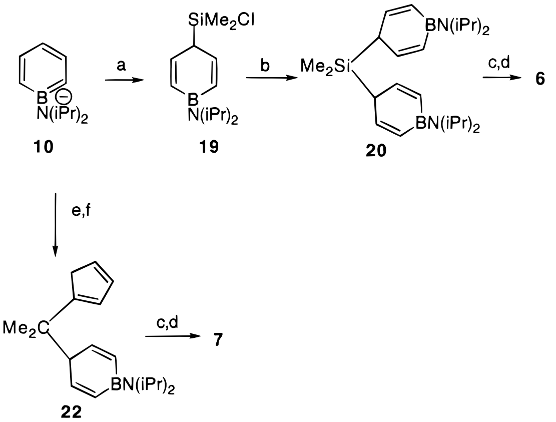
^{a} BCl$_3$. ^{b} HN(iPr)$_2$. ^{c} LDA. ^{d} ZrCl$_4$. ^{e} RX.

Scheme 2. Synthesis of 5^{a}



^{a} BrCH$_2$CH$_2$Br. ^{b} **12a**. ^{c} BCl$_3$. ^{d} HN(iPr)$_2$. ^{e} LDA. ^{f} ZrCl$_4$.

Scheme 3. Synthesis of 6 and 7^{a}



^{a} Me$_2$SiCl$_2$. ^{b} **10**. ^{c} LDA. ^{d} ZrCl$_4$. ^{e} 6,6-Dimethylfulvene. ^{f} H$_2$O.

ligands of **2** could take place at any of the four nonequivalent ring positions. For reasons of simplicity of synthetic design and ease of synthesis, we have initially chosen to explore bridging at C(4).

Compound **2** is easily prepared from the readily available 1,1-dibutyl-1-stannacyclohexa-2,5-diene (**8**)[11] by the sequence of reactions illustrated in Scheme 1.[9,11,12] The scheme is readily adapted for the preparation of 4-substituted boratabenzenes. Treating **8** with LDA in THF affords lithium stannacyclohexadienide (**11**), which can be regioselectively alkylated at C(4) to give **12**.[13,14] Conversion of **12** to the corresponding 4-substituted boratabenzene (**13**) proceeds in the same manner as for the parent compound.

This general method has been successfully employed to prepare **5** as illustrated in Scheme 2. The reaction of **11** with an excess of 1,2-dibromoethane affords **12a** in 40% yield.[13,14] Alkylation of **11** with **12a** gives the ethylene-tethered bis(1,1-dibutylstannacyclohexadiene) (**15**) in 80% yield. This two-step alkylation suppresses the formation of the undesired spiro-compound **14**.[15] Although **15** may be purified by column chromatography, overall yields are higher and it is more convenient to use this product “as is” in subsequent reactions. The exchange reaction of **15** with BCl$_3$ produces **16** and dibutyltin dichloride. The reaction of **16** with excess diisopropylamine gives **17**, which is easily separated from the insoluble diisopropylamine hydrochloride. The reaction of **17** with 2 equiv of LDA produces dianion **18**, which on reaction with ZrCl$_4$ affords the crystalline-bridged boratabenzene complex **5a**. Treating **5a** with methyllithium gave the dimethyl complex **5b**, for which we have obtained a crystal structure.

The silicon-substituted boratabenzene complex **6** has been prepared by a straightforward route involving direct silylation of **10**, as illustrated in Scheme 3. Silylation of **10** with excess dichlorodimethylsilane afforded a high yield of 4-substituted product **19**, which was not detectably contaminated with regioisomers. In contrast, the reaction of lithium 1-methylboratabenzene with Me$_3$SiCl is reported to give largely substitution at C(2).[16] Apparently the bulky diisopropylamino group of **6** prevents attack at the adjacent carbon atoms. Treating **10** with 1 equiv of **19** affords a near quantitative yield of **20**. Reaction of **20** with *tert*-butyllithium followed by ZrCl$_4$ gives **6** as green crystals.

To explore bridged boratabenzene complexes with a one carbon bridge, we have prepared mixed boratabenzene−cyclopentadienyl-bridged zirconium complex **7**. This synthesis is completely analogous to that of an *ansa*-metallocene.[3] The reaction of **10** with 6,6-dimethylfulvene gave an oily mixture of double-bond isomers **22**. No attempt was made to separate these compounds. They were converted to the corresponding dianion by the reaction with LDA. Subsequent reaction with ZrCl$_4$ afforded **7a** in 20% yield. The conversion of **7a** to the dimethyl derivative **7b** was effected in 78% yield by the treatment with methyllithium. Crystals of **7b** suitable for an X-ray diffraction study were obtained from recrystallization from hexane.

Structures

The molecular structures of **5b** and **7b** are illustrated in Figures 1 and 2, respectively. Selected bond distances for **2**,[9] **5b**, and **7b** are collected in Table 1. In each case the geometries of the diisopropylamino-boratabenzene groups are very similar. The corresponding intra-ring C−C and B−C distances vary by no more than 0.02 Å, which indicates that the inter-ring bridging in **5b** and **7b** exerts little perturbation on the boratabenzene groups. Similarly, the juxtaposition of the Zr atoms to the boratabenzene rings is little

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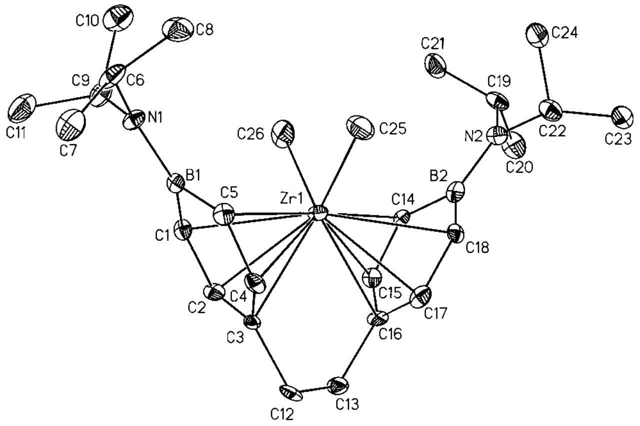


Figure 1. Molecular structure and atom labeling for 5b.

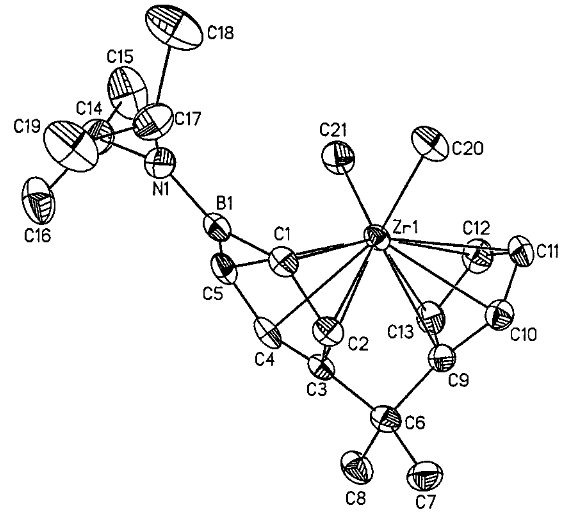


Figure 2. Molecular structure and atom labeling for 7b.

Table 1. Comparison of Selected Distances[a] (Å) and Angles (deg) for 2, 5b, and 7b

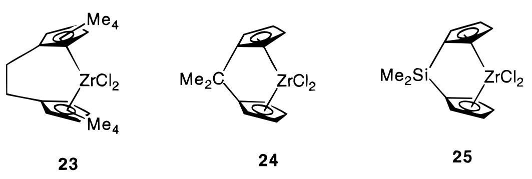
	2	5b	7b
		Distances	
Zr−B	2.980(2)	2.932(16)	2.965(4)
Zr−Cα[b]	2.67(2)	2.680(13)	2.695(5)
Zr−C_β	2.57(2)	2.566(13)	2.541(7)
Zr−Cγ[b]	2.483(5)	2.521(9)	2.474(3)
B−N	1.396(6)	1.426(11)	1.430(5)
B−Cα[b]	1.552(7)	1.545(3)	1.539(5)
Cα−C_β[b]	1.379(7)	1.387(9)	1.388(5)
C_β-C_γ[b]	1.403(7)	1.405(7)	1.424(4)
PLC5−B[c]	0.22(1)	0.11(1)	0.145(2)
		Angles	
PLC5/PhC5	50.4	53	70.5

[a] Average distances. [b] Cα, C_β, Cγ designate the carbon atoms of the boratabenzene rings which are 1, 2 or 1, 3 or 1, 4 to the boron atom, respectively. [c] PLC5 refers to the plane defined by the five carbon atoms of the boratabenzene or the Cp ring.

affected by bridging since the corresponding metal ring atom distances in **2**, **5b**, and **7b** vary by no more than 0.05 Å.

As has been previously discussed for **2**,[9] the Zr atoms of **5b** and **7b** are slip distorted away from the B atoms so that the Zr−B distances (2.93 Å for **5b** and 2.96 Å for **7b**) are too long for effective bonding. Thus the Zr atoms are η^5-bound to the ring C atoms which are coplanar for each ring. However the B atoms are displaced out of these planes away from the metal. In all cases the boron atoms are strongly π-bound to the pendent sp^2-hybridized N.

Chart 2. Structures 23−25



It is interesting to compare the structures of the bridged boratabenzene zirconium complexes with the structures of analogous *ansa*-zirconocenes. In ethylene-bridged zirconocene **23** the dihedral angle between the planes of the permethylated Cp rings is 57°,[17] while the mean planes of the boratabenzene rings of **5b** intersect at 57.6°. However since the boratabenzene rings are not completely coplanar, it may be better to look at the intersection of the planes made by the five carbon atoms of each ring of **5b**, which is 53°. The boratabenzene rings are twisted relative to each other so that the molecule has an approximate C_2 axis through the Zr. The torsional angles of the ethylene bridges are 32° for **23** and 43.7° for **5b**. Thus the bridged boratabenzene is somewhat more twisted than the *ansa*-zirconocene. (See Chart 2 for structures **23**−**25**.)

The Cp ring planes of the $C(CH_3)_2$-bridged zirconocene **24** intersect at an angle of 72°.[18] In **7b** the planes of the Cp ring and that of the five carbon atoms of the boratabenzene intersect at 70.5°. Thus both compounds have nearly identical very wide wedges open to the Zr atoms.

In view of the similarities of **5b** to **23** and **7b** to **24**, it is likely that the structure of **6** is very similar to that found for the identically bridged **25**.[19] Thus we anticipate that the wedge open to the Zr atom in **6** will be close to the 57° found for **25**. However since the $SiMe_2$ bridge should allow little torsion twisting, the bulky diisopropylamino groups of **6** are likely to eclipse each other at the front edge of the open wedge. Thus steric congestion about the Zr atoms should increase in the series **7b** < **5b** < **6**.

Polymerization Studies

It was found that the bridged diisopropylaminoboratabenzene zirconium dichlorides **5a**, **6a**, and **7a**, when activated by excess methylaluminoxane (MAO), were active in the polymerization of mixtures of ethylene and 1-octene. The results are summarized in Table 2. In all cases the products were polyethylene with incoporation of approximately 1% 1-octene. The order of activity was found to be **7a** > **5a** > **6a**. Qualitatively the reactivity decreases as the steric congestion about the metal increases. It is reasonable to propose that greater activity might be found for bridged boratabenzene zirconium complexes analogous to **5a**, **6a**, and **7a** but with smaller groups at boron. An alternative strategy would be to prepare boratabenzene complexes

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Table 2. Summary of Ethylene/1-Octene Polymerization Data for 5a, 6a, and 7a

complex (μmol)	MAO (mmol)	Isopar (g)	1-octene (g)	H_2 (Δpsi)	run time (min)	yield (g)	peak molecular weight	1-octene (mol %)
5a (12.0)	12.0	747	120	26	48	26.1	15 700	1.0
6a (12.0)	12.0	740	123	26	46	9.5	70 300	0.7
7a (3.0)	3.0	743	123	26	30	26.2	83 900	0.7

with the bridging groups at other ring positions. The bridging at the symmetrical C(4) in **5a**, **6a**, and **7a** requires that boron groups occupy the front of the metal wedge. Bridging at any other position would push the boron substituent to the side or rear of the wedge, thus decreasing congestion in the front.

In conclusion we have synthesized bridged boratabenzene complexes of zirconium with one carbon, two carbon, and one silicon bridges. Structurally, these compounds resemble the corresponding *ansa*-zirconocenes. The compounds are active in Ziegler–Natta polymerization of olefins with MAO as a cocataylst.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using a Bruker WH-360, AM-300, or AM-200 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me_4Si, while the ^{11}B NMR spectra were referenced to external $BF_3 \cdot OEt_2$. The combustion analyses were determined by the Analytical Services Department of the Department of Chemistry of the University of Michigan. 1,1-Dibutyl-1-stannacyclohexa-2,5-diene,[11] 1,1-dibutyl-4-(2-bromoethyl)-1-stannacyclohexa-2,5-diene,[13,14] and (*N*,*N*-diisopropyl-1-aminoboratabenzene)lithium[12] were prepared by literature procedures. All other compounds are commercially available.

1,2-Bis(1,1-dibutyl-1-stannacyclohexa-2,5-dien-4-yl)ethane (15). A solution of 1,1-dibutyl-1-stannacyclohexadienyllithium, prepared from 1,1-dibutyl-1-stannacyclohexa-2,5-diene (0.8 g, 2.67 mmol) and 2.67 mmol of lithium diisopropylamide (LDA) in 20 mL of THF, was added to a solution of 1,1-dibutyl-4-(2-bromoethyl)-1-stannacyclohexa-2,5-diene (1.0 g, 2.46 mmol) in 5 mL of THF at −78 °C. After stirring for approximately 16 h, 10 mL of water was added and the product was extracted with pentane. The extracts were dried over $MgSO_4$ and evaporated, leaving a red residue, 1.25 g (81%), of crude product. ^{1}H NMR (C_6D_6): δ 0.9–1.5 (m, Bu), 1.62 (m, CH_2CH_2), 3.11 (m, Hγ), 6.26 (dd, J = 14.2, 1.5 Hz, Hα), 6.61 (dd, J = 14.2, 4.3 Hz, H$_\beta$). ^{13}C NMR (C_6D_6): δ 151.0 (C$_\beta$), 126.4 (Cα), 45.1 (Cγ), 33.7 (CH_2CH_2), 30.0, 27.8, 14.4, 11.4 (Bu). HRMS (EI): calcd for $C_{24}H_{41}{}^{120}Sn_2$ (M-Bu), 569.1252; found, 569.1237.

1,2-Bis(1-chloro-1-boracyclohexa-2,5-dien-4-yl)ethane (16). A solution of 1,2-bis(1,1-dibutyl-1-stannacylohexa-2,5-dien-4-yl)ethane (1.25 g, 2.0 mmol) in pentane was added to a pentane solution of BCl_3 (1.0 g, 8.5 mmol) at −78 °C. After stirring for 2 h at room temperature, the solvent was removed and the product was extracted with pentane. The isolated product contained minor quantities of Bu_2SnCl_2. ^{1}H NMR (C_6D_6): δ 6.51 (m, Hα, H$_\beta$), δ 2.34 (m, Hγ) δ 0.91 (m, CH_2CH_2). ^{13}C NMR (C_6D_6): δ 161.4 (C$_\beta$), 133.9 (Cα), 45.8 (Cγ), 28.3 (CH_2CH_2). ^{11}B NMR (C_6D_6): δ 51.7.

1,2-Bis(*N*,*N*-diisopropyl-1-amino-1-boracyclohexa-2,5-dien-4-yl)ethane (17). 1,2-Bis(1-chloro-1-boracyclohexa-2,5-dien-4-yl)ethane (1.5 g) was treated with excess diisopropylamine in pentane and allowed to stir for 2 h. The solution was filtered, and the filtrate was cooled at −20 °C. Upon standing for several hours, solid formed which was separated from the filtrate. The filtrate was concentrated and allowed to stand at −20 °C for approximately 16 h, during which time more solid separated. The filtrate was separated, and the pentane was removed under reduced pressure, leaving oily product (1.3 g, 58%) which contained small amounts of Bu_2SnCl_2. ^{1}H NMR (C_6D_6): δ 6.73 (d, J = 12.8 Hz, H$_\beta$), 6.55 (d, J = 12 Hz, Hα), 3.69 (m, NCH), 2.82 (m, Hγ), 1.76 (m, CH_2CH_2), 1.12 (d, J = 7.0 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 151.2 (C$_\beta$), 131.3 (Cα), 47.5 (NCH), 43.7 (Cγ), 31.6 (CH_2CH_2), 25.1 (CH_3). HRMS (EI): calcd for $C_{23}H_{39}{}^{11}B_2N_2$(M-$CH_3$), 365.3299; found, 365.3312.

[1,2-Bis(η-*N*,*N*-diisopropyl-1-aminoboratabenzene-4-yl)ethane]zirconium Dichloride (5a). A solution of 1,2-bis(*N*,*N*-diisopropyl-1-amino-1-boracyclohexa-2,5-dien-4-yl)ethane (1.0 g, 2.7 mmol) in ether was treated with 2 equiv of LDA in ether at −78 °C and left to stir for 2 h at room temperature. The resulting suspension was transferred to an ether suspension of $ZrCl_4$ (0.63 g, 2.7 mmol) at −78 °C. The reaction was stirred at 25 °C for about 16 h. Solvent was removed, and the residue was extracted with CH_2Cl_2, treated with pentane, and cooled at −20 °C for 24 h. The crystals formed were collected and washed with pentane. The yield was 0.2 g (14%) based on the estimated purity of the starting material. Mp: 249 °C. ^{1}H NMR (C_6D_6): δ 6.61 (d, J = 11.4 Hz, H$_\beta$), 6.11 (d, J = 11.4 Hz, Hα), 3.75 (m, CHN), 2.52 (s, CH_2CH_2), 1.31 (d, J = 7 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 138 (C$_\beta$), 37.7 (CH_2CH_2), 47.1 (CHN), 23.9 (CH_3). Cα, Cγ not observed. ^{11}B NMR (C_6D_6): δ 30.0. HRMS (EI): calcd for $C_{23}H_{37}{}^{11}B_2{}^{35}Cl_2N_2Zr$(M-$CH_3$), 523.1567; found, 523.1581.

Dimethyl[1,2-bis(η-*N*,*N*-diisopropyl-1-aminoboratabenzene-4-yl)ethane]zirconium (5b). To a suspension of **5a** (0.1 g, 0.18 mmol) in 10 mL of ether was added a solution of MeLi (0.37 mmol) in ether at −78 °C. After stirring 1 h the reaction was allowed to warm to room temperature. Removal of the solvent afforded a yellow residue. The product was extracted with hexane. Cooling to −20 °C afforded 0.07 g (76% yield) of **5b** as yellow crystals, mp 196 °C (dec). ^{1}H NMR (C_6D_6): δ 0.69 (s, ZrMe), 1.39 (s, CH_3), 2.37 (s, CH_2CH_2), 3.53 (m, CH) 6.05 (d, J = 11.3 Hz, Hα), δ 6.15 (d, J = 11.3 Hz, H$_\beta$). ^{13}C NMR (C_6D_6): δ 23.8 (CH_3), 36.9 (CH_2CH_2), 47.0 (CH), 134.0 (C$_\beta$). Cα, Cγ not observed. ^{11}B NMR (C_6D_6): δ 30.0. HRMS (EI): calcd for $C_{26}H_{46}{}^{11}B_2N_2Zr$(M), 498.2594; found, 498.2892.

Chlorodimethyl(*N*,*N*-diisopropyl-1-amino-1-boracyclohexa-2,5-dien-4-yl)silane (19). A solution of butyllithium (2.5 M in hexane, 3.6 mL, 6.98 mmol) was added dropwise with stirring to a solution of (*N*,*N*-diisopropyl-1-amino)boracyclohexa-2,5-diene which had been prepared by reaction of 1,1-dibutyl-1-stannacyclohexadiene and BCl_3 followed by reaction with excess diisopropylamine at 20–25 °C (1.22 g, 6.89 mmol) in THF (10 mL) at −78 °C. The mixture was allowed to warm to 20–25 °C and stirred for 2 h. The mixture was slowly added to dichlorodimethylsilane (8.4 mL, 68.9 mmol) in a Schlenk vessel at −78 °C via cannula. After complete addition, the mixture was warmed to 20–25 °C and stirred for 2 h. The solvent was removed under reduced pressure. Pentane (20 mL) was added, the resulting white suspension was filtered through a sintered glass filter, and the solid was washed with pentane (10 mL). Pentane was removed from the filtrate under reduced pressure to afford product (1.81 g, 98%) as a yellow oil. ^{1}H NMR (300 MHz, C_6D_6): δ 0.22 (s, $SiCH_3$), 1.17 (d, J = 6.9 Hz, $NCH(CH_3)_2$), 3.19 (tt, J = 4.1, 1.0 Hz, H(4)), 3.72 (m, NCH), 6.64 (dd, J = 12.5, 1.0 Hz, H(2,6)), 6.95 (dd, J = 12.5, 4.1 Hz, H(3,5)). ^{13}C NMR (90 MHz, C_6D_6): δ −0.3 ($SiCH_3$), 23.7 (CH_3), 24.0 (CH_3), 44.8 (C(4)), 47.3 (NCH), 132.6 (br, C(2,6)), 144.7 (C(3,5)). ^{11}B NMR (115.5 MHz, C_6D_6): δ

Table 3. Crystal Data and Structure Refinement for 5b and 7b

	5b	7b
empirical formula	$C_{26}H_{46}B_2N_2Zr$	$C_{21}H_{34}BNZr$
formula weight	499.49	402.52
temperature, K	178(2)	178(2)
wavelength, Å	0.710 73	0.710 73
crystal system	monoclinic	monoclinic
space group	$P2(1)/c$ (No. 14)	$P2(1)/c$
unit cell dimensions	$a = 10.808(2)$ Å	$a = 11.0839(14)$ Å
	$b = 16.865(4)$ Å	$b = 11.5600(10)$ Å
	$c = 14.835(3)$ Å	$c = 16.498(2)$ Å
	$\beta = 108.270(10)°$	$\beta = 103.667(8)$
volume, Z	2567.8(9) Å^3, 4	2054.1(4) Å^3, 4
density (calcd), Mg/m^3	1.292	1.302
absorption coefficient, mm^{-1}	0.444	0.537
$F(000)$	1064	848
crystal size, mm	0.22 × 0.20 × 0.04	0.11 × 0.38 × 0.40
θ range for data collection deg	2.82−25.99	2.54−26.00
limiting indices	$-11 \le h \le 13$, $-16 \le k \le 20$, $-18 \le l \le 17$	$-1 \le h \le 13$, $-1 \le k \le 14$, $-20 \le l \le 20$
no. of reflections collected	6291	5165
no. of independent reflections	5049 [R(int) = 0.0557]	4033 [R(int) = 0.0276]
absorption correction	none	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	5013/0/292	4030/0/227
goodness-of-fit on F^2	0.897	0.972
final R indices [$I > 2\sigma(I)$]	R1 = 0.0726, wR2 = 0.1758	R1 = 0.0388, wR2 = 0.0918
R indices (all data)	R1 = 0.1292, wR2 = 0.2013	R1 = 0.0563, wR2 = 0.0963
largest diff peak and hole, e/Å^3	1.881 and −1.156	0.858 and −0.563

31.2. MS (EI) [m/e (intensity)]: 269 (10, M$^+$), 254 (100), 212 (18). MS (EI) exact mass (m/z): calcd for $C_{13}H_{25}{}^{11}BSiN^{35}Cl$(M), 269.1538; found, 269.1535.

Bis(*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)dimethylsilane (20). To a solution of *N,N*-diisopropylaminoboracyclohexa-2,5-diene (1.54 g, 8.70 mmol) in THF (15 mL) at −78 °C was added butyllithium (2.5 M hexane, 3.83 mL, 9.57 mmol). The mixture was allowed to warm to 20−25 °C and stirred for 2 h. The resulting red solution was then added to a solution of (*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)chlorodimethylsilane (2.27 g, 8.70 mmol) in THF (10 mL) at −78 °C. The mixture was stirred for about 16 h at 20−25 °C. Solvent was then removed, and the residue was extracted with pentane (4 × 6 mL). Removal of pentane gave the desired product (4.63 g, 100%) as a yellow solid. A small portion of the product was recrystallized from pentane at −78 °C to give an analytically pure product, mp 100−102 °C. ^1H NMR (300 MHz, C_6D_6): δ −0.13 (s, $SiCH_3$), 1.23 (d, $J = 6.9$ Hz, $NCHCH_3$), 3.20 (t, $J = 4.1$ Hz, H(4)), 3.79 (m, NCH), 6.42 (d, $J = 11.9$ Hz, H(2,6)), 6.90 (dd, $J = 11.5$, 6.2 Hz, H(3,5)). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.6 ($SiCH_3$), 23.67 (CH_3), 24.0 (CH_3), 42.3 46.9 130.3 (br, C(2,6)), 146.0 (C(3,5)). ^{11}B NMR (115.5 MHz, C_6D_6): δ 31.92. MS (El) exact mass (m/z): calcd for $C_{24}H_{44}{}^{11}B_2N_2Si$(M), 410.3461; found, 410.3457. Anal. Calcd for $C_{24}H_{44}B_2N_2Si$: C, 70.31; H, 10.74; N, 6.84. Found: C, 70.27; H, 10.92; N, 7.02.

[Bis(η-*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)dimethylsilane]zirconium Dichloride (6). To a solution of bis(*N,N*-diisopropyl-1-aminoboracyclohexa-2,5-dienyl)dimethylsilane (2.47 g, 5.85 mmol) in ether (17 mL) at −78 °C was added dropwise tBuLi (1.7 M in pentane, 6.89 mL, 11.71 mmol). The mixture was warmed to 20−25 °C and stirred for 2 h, during which time the color changed to dark red. The solution was added dropwise via cannula at −78 °C to a suspension of $ZrCl_4$ (1.37 g, 5.90 mmol) in ether (10 mL). The mixture was gradually warmed to 20−25 °C and stirred for about 16 h. Ether was removed under reduced pressure, and pentane (2 × 5 mL) was added to assist removal of ether. The residue was extracted with dichloromethane (3 × 8 mL), and the extracts were filtered through a sintered glass filter. The filtrate was concentrated and recrystallized at −78 °C to give the desired product (2.15 g, 63%) as a green solid, mp 152−153 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (s, $SiCH_3$), 1.24 (d, $J = 6.8$ Hz, $NCHCH_3$), 1.25 (d, $J = 6.8$ Hz, $NCHCH_3$), 3.75 (m, NCH), 6.35 (d, $J = 11.2$ Hz, H(2,6)), 6.98 (d, $J = 11.2$ Hz, H(3,5)). ^{13}C NMR (90 MHz, $CDCl_3$–C_6D_6): δ −5.3 ($SiCH_3$), 23.5 (CH_3), 23.8 (CH_3), 46.7 (NCH), 91.4 (C(4)), 134.2 (br, C(2,6)), 139.3 (C(3,5)). ^{11}B NMR (115.5 MHz, C_6D_6): δ 29.9. MS (EI) exact mass (m/z): calcd for $C_{23}H_{39}{}^{11}B_2{}^{35}Cl_2N_2SiZr$([M−$CH_3$]), 553.1493; found, 553.1497.

2-(Cyclopentadienyl)-2(*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)propane (22). A solution of 6,6-dimethylfulvene (0.6 g, 5.7 mmol) in 5 mL of THF was added to (*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)lithium, which had been prepared from *N,N*-diisopropyl-1-amino-1-boracyclohexa-2,5-diene (1.0 g, 5.6 mmol) and BuLi (7.3 mmol), at −78 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. To the resulting red solution was added 1 mL of water, and the solvent was removed under reduced pressure. The residue was extracted with pentane. The extracts were dried over $MgSO_4$, and the solvent was removed, leaving an oily residue, 1.0 g (62%) of crude product. The ^1H NMR indicated a mixture of isomers. HRMS (EI): calcd for $C_{19}H_{30}{}^{11}BN$(M), 283.2471; found, 283.2468.

[2-(η-Cyclopentadienyl)-2-(η-*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)propane]zirconium Dichloride (7a). A solution of dilithium salt of 2-(cyclopentadienyl)-2-(*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)propane (prepared from 0.8 g (2.8 mmol) of **22** and 5.6 mmol of LDA) in ether was added to 0.65 g (2.8 mmol) of $ZrCl_4$ in ether at −78 °C. The reaction mixture was stirred at 20−25 °C for about 16 h. The solvent was removed under reduced pressure, and the residue was washed with pentane. The remaining residue was extracted with toluene and treated with pentane. Upon standing about 16 h in the freezer, microcrystalline product formed, which was washed with pentane and dried, giving 0.3 g (24%) of **7a**, mp 234 °C. ^1H NMR (C_6D_6): δ 6.71 (d, $J = 12.1$ Hz), 6.51 (d, $J = 12.1$ Hz) 6.3, (m, Cp), 5.0 (m, Cp), 3.88 (m, CHN), 1.12 (s, CMe_2), 1.12 (d, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 133.2 (C_β), 124.1 (Cp), 104.2 (Cp), 60.4 (CMe_2), 47.0 (NCH), 30.5 ($CHMe_2$), 23.5 (CH_3); Cα not observed. ^{11}B NMR (C_6D_6): δ 27.3. HRMS (EI): calcd for $C_{18}H_{25}{}^{11}B^{35}Cl_2NZr$(M−$CH_3$), 426.0504; found, 426.0524.

Dimethyl[2-(η-cyclopentadienyl)-2-(η-*N,N*-diisopropyl-1-aminoboratabenzene-4-yl)propane]zirconium (7b). To a suspension of 0.1 g (0.22 mmol) of **7a** in 10 mL ether was added 0.45 mmol MeLi in ether at −78 °C. After stirring 1 h the reaction was allowed to warm to room temperature.

Removal of the solvent afforded a yellow residue, which was extracted with hexane. Cooling the extracts to −20 °C afforded yellow crystals, 0.06 g (66%), mp 175 °C (dec). ^{1}H NMR (C_6D_6): δ 0.36 (s, ZrMe), 1.08 (s, CMe$_2$) 1.34 (CH$_3$), 3.81 (m, CH), 4.91, 6.22 Cp (observed as triplets), 6.36 (2 overlaping doublets, J = 12.1 Hz). ^{13}C NMR (C_6D_6): δ 23.5 (Me), 46.8 (CH), 25.5 (CMe$_2$), 32.0 (Me$_2$*C*), 102.8 (Cα(Cp)), 115.6 (C$_\beta$(Cp)), 117.8 (Ci(Cp)), 132.9 (C$_\beta$); ZrMe, Cα, Cγ not observed. ^{11}B NMR (C_6D_6): δ 27.8. HRMS (EI): calcd for $C_{21}H_{34}{}^{11}BNZr$(M), 401.1831; found, 401.1850.

Ethylene/Octene Copolymerization. A 2 L reactor is charged with mixed alkane solvent (Isopar-E) and 1-octene. Hydrogen is added by differential pressure expansion from a 75 mL addition tank from 300 psig (2.1 MPa) to near 275 psig (1.9 MPa). The reactor and contents are then heated to and maintained at 140 °C, the polymerization temperature, and saturated with ethylene at 500 psig (3.4 MPa). In an inert atmosphere glovebox the appropriate quantities of metal complex and methylalumoxane (MAO) cocatalyst solutions (0.005 00 and 1.5 M, respectively, in toluene) are combined, and this catalyst solution is transferred to a catalyst addition tank. The polymerization is initiated by injecting this catalyst solution into the contents of the reactor. The polymerization conditions are maintained for the run time with ethylene provided on demand at 500 psig (3.4 MPa). Additional catalyst solution prepared and transferred in the same way may be added to the reactor throughout the course of the reaction. The polymer solution is removed from the reactor and combined with a hindered phenol antioxidant and isopropyl alcohol. Volatile components are removed from the polymer in a vacuum oven set at 140 °C for about 20 h. The dried polymers were analyzed by ^{13}C NMR spectroscopy and GPC. Results are contained in Table 2.

X-ray Structure Determinations. Crystals of **5b** and **7b** suitable for X-ray diffraction were obtained by recrystallization from hexane. Crystallographic data are collected in Table 3. ORTEP drawings of **5b** and **7b** showing the numbering schemes used in refinement are illustrated in Figures 1 and 2, respectively. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: Tables of bond distances, angles, positional paramters, anisotropic thermal parameters, and hydrogen atom coordinates of **5b** and **7b** (13 pages). Ordering information is given on any current masthead page.

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