Organometallics **2003,** *22,* 203−206 203

ansa-Bis(1-boratabenzene) Zirconium(IV) Complexes with Short Carbon Bridges to Boron

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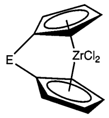
*Summary: The reaction of 1,1-dibutyl-1-stannacyclohexa-2,5-diene (**8**) with 1,2-bis(dichloroboryl)benzene **9** affords exchange product **10**, which on deprotonation followed by reaction with $ZrCl_4$ gives the very labile o-phenylene-bridged bis(1-boratabenzene)zirconium dicholoride **6**. A similar reaction sequence from **8** and 1,1-bis(dichloroboryl)-2-methyl-1-propene **11** affords the 1,1-isobutenyl-bridged bis(1-boratabenzene)zirconium dichloride **7**. The X-ray structure of **7** is described.*

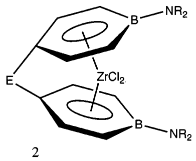
Bridged or *ansa*-zirconocene dihalides **1** have been extensively studied.[1−4] Small bridging groups, e.g., in **1a**, pinch back the rings, which opens the wedge between the rings, making the metal more accessible. The bridge also constrains rotation about the ring−metal axis, which limits conformational mobility. The major interest in structures **1** has been that certain *ansa*-zirconocene derivatives are highly active and stereoselective catalysts for the polymerization of olefins[5] and for organic synthesis.[6]

Since boratabenzenes can serve as surrogates for Cp in metallocenes,[7,8] it was of interest to prepare bridged boratabenzene zirconium complexes. In prior work we prepared bis(boratabenzene) zirconium complexes (**2a** and **2b**) and a mixed Cp, boratabenzene zirconium complex, **3**, which are bridged at the C(4) position.[9] Complexes **2** and **3** have structures that are closely analogous to the corresponding *ansa*-zirconocenes. Bazan and co-workers have examined the *trans*-1,2-cyclohexanedioxy-bridged bis(boratabenzene) zirconium complex **4**,[10a] while we have prepared bis(boratabenzene) zirconium complex **5**, in which the boron atoms are bridged by a dimethylethylenediamino group.[10b] To examine complexes with smaller bridging groups at boron, we have now prepared **6** and **7**.



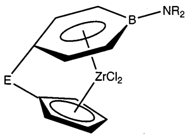
1

a E = CMe$_2$



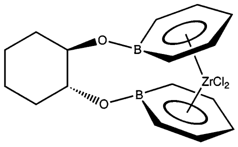
2

a E = CH$_2$CH$_2$
b E = SiMe$_2$

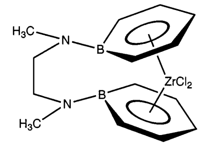


3

a E = CMe$_2$



4



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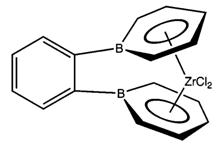
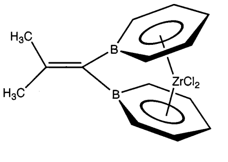


6



7

Results and Discussion

Boratabenzenes are most conveniently prepared by the reaction of stannacyclohexadiene **8** with the appropriate boron dihalide followed by deprotonation.[11] Since bis(dichloroboryl) derivatives **9** and **11** have been used by Kaufmann[12] and Siebert[13] to prepare diboron-containing heterocycles, they appeared to be attractive starting materials for the preparation of **6** and **7**. We find that the reaction of the 1,2-bis(dichloroboryl)benzene **9**[12] with 2 mol of **8** affords a 60% yield of the

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(1) (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. Ryan, E. J. In *Comprehensive Organometallic Chemistry II*; Lappert, M. F., Ed.; Pergamon: Oxford, UK, 1995; Vol. 4, p 483.

(2) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (c) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(3) (a) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1970**, 2497. (b) Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175.

(4) Wiesenfeldt, H.; Reimuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359.

(5) For recent reviews, see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, Germany, 1995. (c) Coates, G. W.; Waymouth, R. M. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, p 1193. (d) Aulbach, M.; Küber, F. *Chem. Unserer Zeit* **1994**, *28*, 197. (e) Janiak, C. Metallocene Catalysts for Olefin Polymerization. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 547−623. (f) Gladysz, J. A. *Chem. Rev.* **2000**, *100*, 1167−1682.

(6) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1263.

(7) (a) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1982; Vol. 1, p 381. (b) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199. (c) Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Housecroft, C. E., Ed.; Pergamon: Oxford, UK, 1995; Vol. 1, p 197. (d) Fu, G. *Adv. Organomet. Chem.* **2001**, *47*, 101.

(8) For recent work on boratabenzenes see: (a) Zheng, X.; Wang, B.; Herberich, G. E. *Organometallics* **2002**, *21*, 1949. (b) Hoic, D. A.; DiMare, M.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 7155. Tweddell, J.; Hoic, D. A.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 8286. (c) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 1365. (d) Komon, Z. J. A.; Rogers, J. S.; Bazan, G. C. *Organometallics* **2002**, *21*, 3189.

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

(10) (a) Rogers, J. S.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 1288. (b) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **2001**, *20*, 468.

(11) (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (b) Ashe, A. J., III; Chan, W. T. *J. Org. Chem.* **1979**, *44*, 1409.

(12) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901.

(13) Siebert, W.; Hildenbrand, M.; Hornbach, P.; Karger, G.; Pritzkow, H. *Z. Naturforsch.* **1989**, *44b*, 1179.

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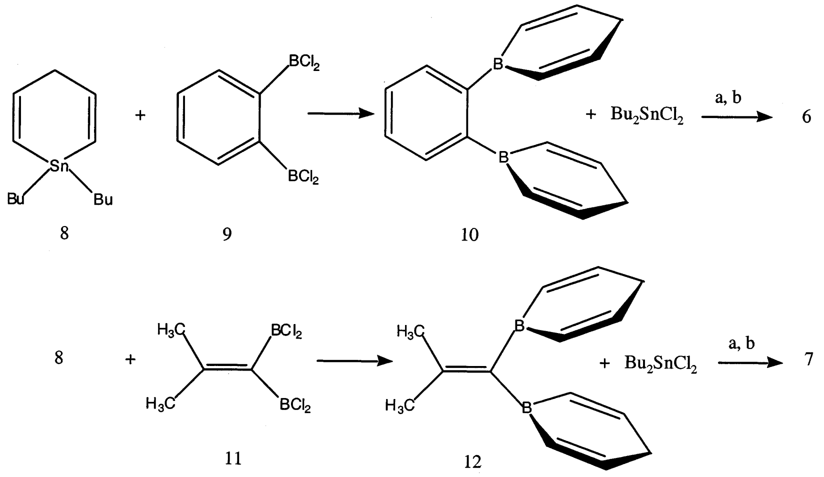
Scheme 1[a]



[a] Key: a, LDA; b, $ZrCl_4$.

desired exchange product **10** mixed with Bu_2SnCl_2. Since separation of **10** from Bu_2SnCl_2 proved difficult, the mixture was treated directly with excess LDA in ether, which was followed by reaction with 1 equiv of $ZrCl_4$. Complex **6** could be isolated only in poor yield (7%) as a bright yellow solid. The ^1H, ^{11}B, and ^{13}C NMR and high-resolution mass spectra were consistent with assignment of the product as **6**. However, it was noted that solutions of **6** quickly formed intractable decomposition products. Similarly, storage of solid **6** at low temperatures led to decomposition. The lability of **6** is consistent with the low yield in its preparation. These difficulties led us to look for more tractable boron-bridged complexes.

The reaction of **8** with 2 equiv of **11**[13] afforded a 95% yield of **10** mixed with Bu_2SnCl_2. As in the previous case, it was found to be difficult to separate the two products by distillation. However, treating the mixture with excess LDA in ether followed by $ZrCl_4$ afforded a 48% yield of crystalline **7**. The ^1H, ^{11}B, and ^{13}C NMR spectra of **7** are similar to those of **6** and other boratabenzene zirconium complexes.[14–18] Fortunately, **7** displayed none of the lability of **6** and was easily handled using Schlenk and drybox techniques.

The short bridge of **7** suggested that it should be a highly strained molecule, which might have an interesting structure. Crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2. The molecular structure is illustrated in Figure 1 with the appropriate atom-labeling scheme. The molecule has a crystallographically imposed mirror plane, which bisects the Cl–Zr–Cl bond angle and passes through the zirconium and boron atoms, the bridging atoms, and C(3) and C(6).

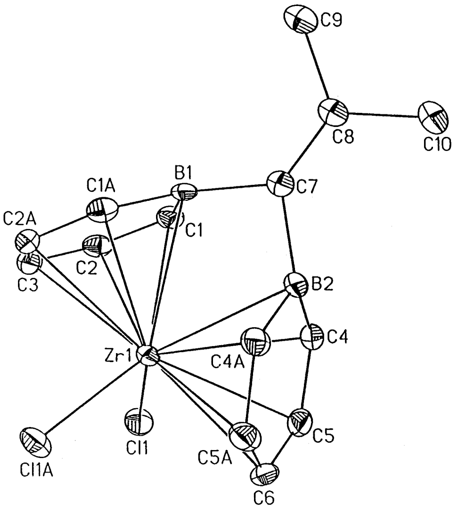


Figure 1. Molecular structure and atom labeling for **7**.

Table 1. Comparison of Selected Average Distances (Å) and Angles (deg) for 7 and 13[a]

	7	13
	Distances	
Zr–Cl	2.4269(7)	2.431(6)
Zr–B	2.687(9)	2.814(4)
Zr–C_α[b]	2.604(4)	2.631(4)
Zr–C_β[b]	2.662(3)	2.572(2)
Zr–C_γ[b]	2.592(10)	2.526(1)
B–C_{exo}	1.597(5)	1.57(1)
B–C_α	1.528(6)	1.523(1)
C_α–C_β	1.398(4)	1.383(1)
C_β–C_γ	1.405(4)	1.380(2)
PLC5–B[c]	+0.032(9)	−0.12(5)
PLC5–Zr[c]	+2.184(3)	+2.182(5)
	Angles	
PLC5/PLC5′[c]	59.4(1)	50.4
B–C–B	95.4(1)	

[a] Ref 15. [b] C_α, C_β, and C_γ designate the carbon atoms which are 1,2-, 1,3-, and 1,4- relative to the boron atom, respectively. [c] PLC5 refers to the plane defined by the five carbon atoms of the boratabenzene ring.

It is useful to compare structure **7** with that of the nonbridged bis(1-methylboratabenzene) zirconium dichloride **13**.[15] Selected bond distances and other structural parameters of **7** and **13** are collected in Table 1. The intra-ring bond distances are little effected by the bridging since the corresponding B–C and C–C bond

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(14) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1997**, *118*, 2291. (b) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492.

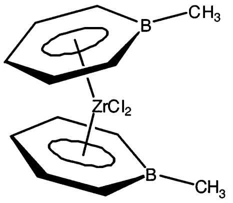
(15) Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751.

(16) Herberich, G. E.; Englert, U.; Ganter, B.; Pons, M. *Eur. J. Inorg. Chem.* **2000**, 979.

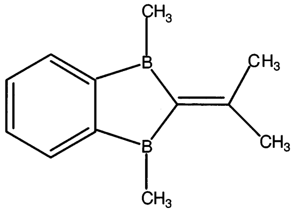
(17) (a) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (b) Barnhart, R. W.; Bazan, G. C.; Mourey, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (c) Bazan, G. C.; Cotter, W. D.; Komon, Z. J. A.; Lee, R. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1371. (d) Bazan, G. C.; Lee, R. A. *J. Organomet. Chem.* **2002**, *642*, 275.

(18) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466.

distances of **7** and **13** vary by no more than ±0.02 Å. The boratabenzene rings of **7** are close to planar, with a small displacement (0.03 Å) of the boron atoms of **7** out of the plane of the five ring carbon atoms toward the metal. In this respect the structure of **7** is unique. In **13** and in all other structurally characterized boratabenzene metal complexes the boron atoms are displaced away from the metal.[10,14−18] The bridging also distorts the B−C−B angle (95.4°), which is reduced by 10° from that of **14** (105.4°).[13] However, the B−C bond distances of **7** and **14** are virtually identical.



13



14

The distances of the Zr atoms to the boratabenzene ring atoms are considerably different for **7** than for **13**. In **13** and in all other structurally characterized boratabenzene zirconium(IV) complexes[10,14−18] the Zr atom is much closer to the five ring carbon atoms that to boron. In cases where the boron bears a π-donor substituent,[14a] e.g., **2a**[9] and **3**,[9] η^5-bonding is indicated. It has been argued that the electrophilic Zr(IV) atoms prefer coordination to the more electron-rich carbon atoms.[14] In contrast, the Zr atom of **7** is rather evenly coordinated to the ring since the metal−ring atom distances vary by no more than ±0.09 Å. Clearly, this more symmetrical bonding is enforced by the bridge.

The major modification of the structure of *ansa*-zirconocenes relative to nonbridged zirconocenes is the greater canting of the rings. The dihedral angle between the Cp planes in Cp_2ZrCl_2 is 52°, which increases to 72° for $C(CH_3)_2$-bridged **1a**. The dihedral angle between the mean planes of the boratabenzene rings of **7** is 58.7°.[19] The wedge to Zr is considerably less open for **7** than for **1a**, even though both complexes have a one carbon bridge. The major reason for the smaller canting in **7** is probably the η^6-coordination of its larger boratabenzene ring. For all six atoms of each of the more extended boratabenzene rings to be within bonding distance to Zr, the angle between the rings must contract. An additional comparison can be made with **3**, in which the plane of the Cp ring and that of the five carbon atoms of the η^5-coordinated boratabenzene intersect at 70.5°. Complex **3** resembles **1a** more than **7** in its degree of canting. Apparently, the position of the bridge as well as its size influences the structure of boratabenzene complexes.

In summary, we have prepared *ansa*-bis(boratabenzene) zirconium complexes with one and two carbon atom bridges. The structure of **7** shows that the boratabenzene rings are η^6-coordinated. This has the effect of constricting the ring−metal−ring wedge relative to η^5-coordinated boratabenzene zirconium complexes.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried using standard procedures. The mass spectra were determined using a VG-70-S spectrometer. The NMR spectra were obtained using either a Bruker WH 400, WH 300, or AM 300 spectrometer. The ^1H NMR spectra and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to $SiMe_4$. The ^{11}B NMR spectra were referenced to external BF_3-OEt_2.

1,1-Dibutyl-1-stannacyclohexa-2,5-diene,[11] 1,2-bis(dichloroboryl)benzene,[12] and 1,1-bis(dichloroboryl)-2-methyl-1-propene[13] were prepared by literature procedures. All other compounds are commercially available.

1,2-Bis(1-boracyclohexa-2,5-dienyl)benzene, 10. A solution of 1,1-dibutyl-1-stannacyclohexa-2,5-diene (5.70 g, 19.1 mmol) in 10 mL of pentane was added dropwise to a solution of **9** (1.85 g, 7.73 mmol) in 10 mL of pentane at −78 °C. After stirring for 10 min at −78 °C, the reaction mixture was allowed to warm to 25 °C and was stirred for 8 h. The reaction mixture was then cooled to −30 °C, causing a solid to precipitate under a clear solution. The solution was drawn off via cannula. The solvent was removed in vacuo, leaving a mixture of **10** and Bu_2SnCl_2, which were difficult to separate. The total weight of the mixture was 2.55 g (60% yield of **10** estimated using ^1H NMR spectroscopy). ^1H NMR (C_6D_6): δ 7.93 (m, 2H, ArH); 7.37 (m, 2H, ArH); 7.00 (br m, 8H, C*H*C*H*B); 2.69 (t, $J = 1.6$ Hz, 4H, CH_2); 1.5−0.5 (m, Bu). ^{11}B NMR (C_6D_6): δ 52.0.

(Bis-1,2-(η-1-boratabenzene)benzene)zirconium Dichloride, 6. A solution of LDA (7.70 mmol) in ether was added to an ether solution of **10** that contained Bu_2SnCl_2 (3.62 mmol) at −78 °C. After stirring for 10 min at −78 °C, the solution was allowed to warm to 25 °C and was stirred for 45 min. The solvent was then removed under reduced pressure, and the residue was washed with 65 mL of pentane. The solid residue was dissolved in 25 mL of ether, which was then added to a suspension of $ZrCl_4$ (0.82 g, 3.52 mmol) in 7 mL of ether at −78 °C. The yellow-orange mixture was stirred cold 1 h and then was allowed to warm slowly to 25 °C over 11 h. The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2. Extracts were filtered through Celite, concentrated, and cooled to −30 °C. After addition of pentane a precipitate formed. The precipitate was isolated, washed with pentane, and dried in vacuo, giving 0.10 g (7%) of a bright yellow solid, mp 112−114 °C. The product decomposed on storing in dry ice after 36 h. ^1H NMR (C_6D_6): δ 7.54 (m, 2H, ArH); 7.44 (dd, $J = 10.3$, 7.1 Hz, 4H, H_β); 7.40 (m, 2H, ArH); 6.51 (tt, $J = 7.1$, 1.5 Hz, 2H, H_γ); 5.98 (dd, $J = 10.3$, 1.5 Hz, 4H, H_α). ^{13}C NMR (C_6D_6): δ 151.5, 129.2, 126.8, 114.6. (Signals for carbon atoms adjacent to B were not observed.) ^{11}B NMR (C_6D_6): δ 41.6. HRMS(EI) calcd for $C_{16}H_{14}{}^{11}B_2{}^{35}Cl_2Zr$: 387.9706. Found: 387.9721. Attempted recrystallization from a mixed pentane/CH_2Cl_2 solvent led to decomposition.

Bis-1,1-(1-boracyclohexa-2,5-dienyl)-2-methyl-1-propene, 12. A solution of 1,1-dibutyl-1-stannacyclohexa-2,5-diene (9.75 g, 32.64 mmol) in 45 mL of pentane was added dropwise to a solution of **11** (3.55 g, 16.33 mmol) in 20 mL of pentane at −78 °C. After the addition was complete the reaction mixture was allowed to warm slowly to 25 °C and was stirred for 12 h. The reaction mixture was then cooled to −30 °C for 3 h, causing a white solid to precipitate under a yellow solution. The solution was drawn off via cannula, and the solvent was removed in vacuo, leaving a mixture of **12** and Bu_2SnCl_2, which were difficult to separate. The total weight of the mixture was 8.61 g (95% yield of **12** estimated using ^1H NMR spectroscopy). ^1H NMR ($CDCl_3$): δ 7.20 (dt, $J = 11.9$, 3.0 Hz, 4H, H_β); 6.72 (dt, $J = 11.9$, 1.6 Hz, 4H, H_α); 3.12 (m, 4H, CH_2); 1.90−1.65 (m, 32H, Me, Bu), 1.5−0.7 (m, Bu). ^{13}C NMR (C_6D_6): δ 168.0, 152.0, 138.0 (B*C*H), 36.8, 27.6 (Bu), 26.7, 26.4 (Bu), 22.7 (Bu), 13.9 (Bu). (CB_2 not observed.) ^{11}B NMR ($CDCl_3$): δ 52.7.

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[19] Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

Table 2. Crystal Data and Structure Refinement Details for 7

empirical formula	$C_{14}H_{16}B_2Cl_2Zr$
fw	368.01
temp, K	158(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$c2/m$
unit cell dimens	
a, Å	14.5922(9)
b, Å	9.9618(6)
c, Å	10.8059(7)
β, deg	103.1620(10)
V, Å^3, Z	1529.5(2), 4
calcd density, Mg/m^3	1.598
abs coeff, mm^{-1}	1.049
$F(000)$	736
cryst size, mm	0.06 × 0.06 × 0.14
limiting indices	$-19 \leq h \leq 19$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
no. of reflns collected	8091
no. of indep reflns	2051
abs corr	semiempirical from equivalents
refinement method	full-matrix least-squares on $F(2)$
no. of data/restraints/params	2029/0/137
GOF on F^2	1.091
final R indices ($I > 2\sigma(I)$)	R1 = 0.0378, wR2 = 0.0591
R indices (all data)	R1 = 0.0584, wR2 = 0.0652
largest diff peak and hole, e/Å^3	0.568 and −0.472

(Bis-1,1-(η-1-boratabenzene)-2-methyl-1-propene)zirconium Dichloride, 7. To a solution of **12** (0.67 g, 3.20 mmol) contaminated with Bu_2SnCl_2 (3.30 mmol) in 10 mL of ether at −78 °C was added LDA (10 mL, 12.3 mmol) dropwise via cannula, giving a bright yellow solution. After stirring cold for 2 h the reaction was allowed to warm to 25 °C, giving an orange solution. After 3 h, the solvent was removed under vacuum and the residue was washed with a total of 40 mL of pentane. After drying the dianion in vacuo solid $ZrCl_4$ (0.76 g, 3.26 mmol) was added. The reaction mixture was cooled to −78 °C, and 25 mL of ether was added slowly. The reaction mixture was allowed to warm slowly to 25 °C with stirring over 12 h. The solvent was removed in vacuo, and the residue was extracted with toluene. The extracts were filtered through Celite, and the solvent was removed under reduced pressure. The residue was washed with pentane and dried to give 0.48 g (48%) of a yellow solid, mp 156−158 °C. ^{1}H NMR (C_6D_6): δ 7.35 (dd, J = 10.5, 7.1 Hz, 4H, H_β); 6.33 (tt, J = 7.06, 1.5 Hz, 2H, H_γ); 6.14 (dd, J = 10.5, 1.5 Hz, 4H, H_α); 2.13 (s, 6H, Me). ^{13}C NMR (C_6D_6): δ 150.3, 134.0 (B*C*H), 110.0, 26.9. (Signals for acyclic vinyl carbon atoms were not observed.) ^{11}B NMR (C_6D_6): δ 35.6. HRMS calcd for $C_{14}H_{16}{}^{11}B_2{}^{35}Cl_2Zr$: 365.9862. Found: 365.9849. Satisfactory CH analysis could not be obtained; however, the H NMR spectrum indicated good purity. Single crystals suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 solution cooled to −30 °C.

X-ray Structure Determination. Crystallographic data for **7** are collected in Table 2. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: Details of the X-ray study of **7** and NMR spectra of **6**, **7**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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