

Anionic *ansa*-Zirconocenes with Pentafluorophenyl-Substituted Borato Bridges

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The *ansa*-borane complex $(\text{Me}_2\text{S})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (**1**) reacts selectively with 2 equiv of LiC_6F_5 to give $(\text{Me}_2\text{S})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (**2**) and with 3 equiv LiC_6F_5 to form the borato-bridged complex $[\text{Li}(\text{Et}_2\text{O})_3][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (**3a**). The C_6F_5 groups are exchanged for Me by reaction with AlMe_3 to form $[\text{Li}(\text{Et}_2\text{O})_x][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (**4**). Treatment of BCl_3 with $(\text{SiMe}_3)(\text{SnMe}_3)\text{C}_5\text{H}_4$ affords $\text{BCl}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ (**5**), which undergoes a dehalosilylation reaction with $\text{ZrCl}_4(\text{Me}_2\text{S})_2$ to give $\text{Cl}(\text{Me}_2\text{S})\text{B}(\text{C}_5\text{H}_4)\text{ZrCl}_2$ (**6**). The reaction of **6** with LiC_6F_5 proceeds in a fashion similar to that of **2**, leading first to $(\text{Et}_2\text{O})\text{ClB}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (**7**) and with 5 equiv of LiC_6F_5 to $[\text{Li}(\text{Et}_2\text{O})_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (**9a**) in 28% yield. The yield is improved through the use of $\text{C}_6\text{F}_5\text{MgBr}$ at 60 °C. The C_6F_5 groups are readily exchanged for Me through reaction with LiMe to give $[\text{Li}(\text{Et}_2\text{O})_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (**10a**). Complexes **3**, **9**, and **10** are catalysts for ethene polymerization when activated with MAO or $\text{AlBu}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$.

Introduction

As is now well established,¹ the active species in metallocene-based olefin polymerization catalysts are electron-deficient cationic metallocene alkyl complexes of the type $[\text{Cp}_2\text{MR}]^+$ (Chart 1, structure I), which are stabilized by weakly coordinating anions such as $[\text{MeMAO}]^-$ or $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.^{2–6} This has sparked interest

by us and others in modifying the structure of the active species (or its immediate precursor complex) by exploring electrically neutral analogues and zwitterionic structures where the anionic component is covalently attached to the cationic species. Examples are complexes with borato-substituted cyclopentadienyl ligands, as in **II**⁷ and **III**,⁸ “self-activating” complexes containing Lewis-acidic Cp substituents as in **IV**,⁹ Erker’s allylic zwitterion **V**,¹⁰ half-sandwich complexes of type **VI**,¹¹ and complexes with dianionic ligands such as boroles (**VII**)^{11d,12} and trimethylenemethane complexes (**VIII**).¹³ A long-term aim of our research has been the synthesis of zwitterionic *ansa*-metallocenes where the weakly

(1) For reviews see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (c) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(2) (a) Turner, H. W. Eur. Patent Appl. 0277 004, 1988. (b) Ewen, J. A.; Elder, M. J. Eur. Patent Appl. 0426 637, 1990. (c) Ewen, J. A.; Elder, M. J. Eur. Patent Appl. 0427 697, 1991. (d) Yang, X.; Stern, C. L. Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (e) Ewen, J. A.; Elder, M. J. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 179. (f) Ewen, J. A. *Stud. Surf. Sci. Catal.* **1994**, *89*, 405.

(3) (a) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135. (b) Chen, Y. X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (c) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842. (d) Chen, Y. X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (e) Chen, Y. X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582. (f) Chen, Y. X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (g) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996. (h) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312.

(4) For related boranes see: (a) Köhler, K.; Piers, W. E. *Can. J. Chem.* **1998**, *76*, 1249. (b) Köhler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Brasakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557. (c) Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244. (d) Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695. (e) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619.

(5) Delocalized diborate anions have been described: (a) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533. (b) LaPointe, R. E. WO 99/42467, 1999. (c) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560. (d) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223.

(6) Zwitterionic alternatives to cationic active species have been discussed, see: (a) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 1. (b) Piers, W. E.; Sun, Y.; Lee, L. W. M. *Top. Catal.* **1999**, *7*, 133.

(7) (a) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (b) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829. (c) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (d) Burlitch, J. M.; Burk, J. H.; Leonowicz, M. E.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1702. (e) Braunschweig, H.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1613. (f) Bohra, R.; Hitchcock, P. B.; Lappert, M. F.; Au-Yeung, S. F.; Leung, W. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2999.

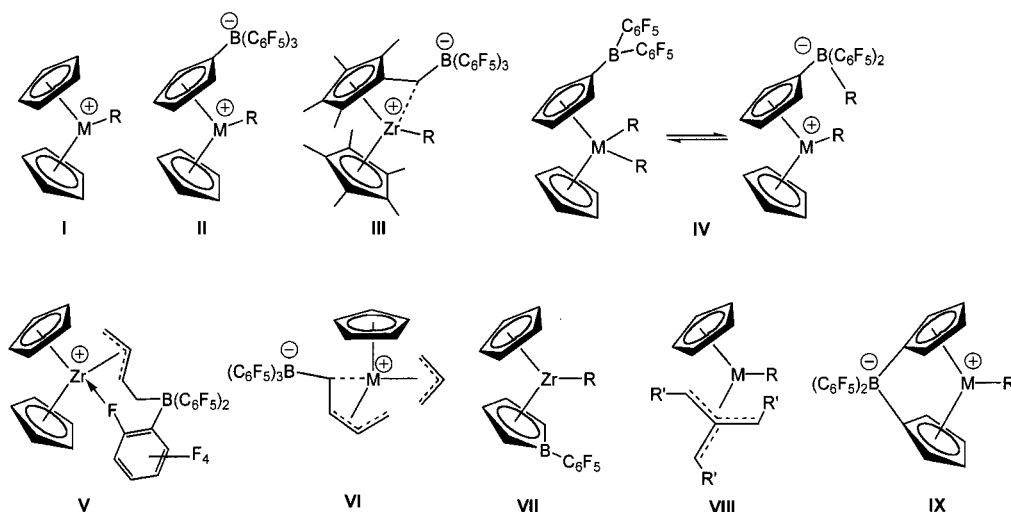
(8) (a) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. (b) Song, X.; Bochmann, M. *J. Organomet. Chem.* **1997**, *545–546*, 597.

(9) (a) Reetz, M. T.; Brümmer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501. (b) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995. (c) Lancaster, S. J.; Al-Benna, S.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1599.

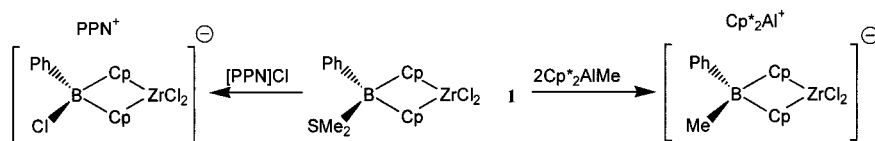
(10) (a) Temme, B.; Erker, G.; Karl, J.; Luftmann, R.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (b) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165. (c) Karl, J.; Erker, G. *J. Mol. Catal. A: Chem.* **1998**, *128*, 85. (d) Karl, J.; Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **1998**, *120*, 5643.

(11) (a) Jiménez Pindado, G.; Thornton-Pett, M.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358. (b) Jiménez Pindado, G.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115. (c) Jiménez Pindado, G.; Thornton-Pett, M.; Hursthouse, M. B.; Coles, S. J.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1999**, 1663. (d) Jiménez Pindado, G.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816. (e) Corradi, M. M.; Jiménez Pindado, G.; Sarsfield, M. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1150.

Chart 1



Scheme 1



coordinated anion is incorporated into the bridge, to give compounds of type **IX**. Early attempts to access such structures using preformed bis(cyclopentadienyl)borates $[(C_6F_5)_2B(C_5H_5)_2]^-$ had not been successful since these borato ligands proved elusive. We report here an alternative route to complexes of type **IX**.

A number of groups have reported the synthesis of boron-bridged *ansa*-metallocene complexes. The complexes can be broadly divided into two classes: (i) zirconocenes bridged by aminoboryl moieties where the electrophilicity of boron is attenuated by partial π -bonding to nitrogen;¹⁴ and (ii) zirconocenes bridged with Lewis-acidic boryl linkages.^{15,16} These offer the prospect of coordinating Lewis-basic ligands to boron. However, in the absence of strongly coordinating donors such as PMe_3 these complexes proved unstable toward alkylation.¹⁵

Very recently, while this work was in progress, Shapiro has reported the first synthesis of borato-bridged *ansa*-metallocenes by the reaction of $(Me_2S)(C_6H_5)B(C_5H_4)_2ZrCl_2$ (**1**) with $PPNCl$ or Cp^*_2AlMe to give $[PPN][Cl](C_6H_5)B(C_5H_4)_2ZrCl_2$ and $[Cp^*_2Al][Me](C_6H_5)B(C_5H_4)_2ZrCl_2$, respectively (Scheme 1).¹⁷

An alternative strategy to first synthesizing a borato-bis(cyclopentadienyl) ligand is the preparation of *ansa*-borane complexes of the type that Shapiro and others have made, followed by their subsequent conversion to *ansa*-borates (structure **IX**). We believed that the ideal bridging group would be $[-B(C_6F_5)_2-]$, which, from our experience of the tetrakis(pentafluorophenyl)borate anion chemistry, should have greater stability toward electron and ligand transfer than the known $-BPh(Cl)-$ and $-BPh(Me)-$ bridged examples.

We report here the synthesis of bis(pentafluorophenyl)borato-bridged *ansa*-zirconocene complexes and their alkylation products.

Results and Discussion

The *ansa*-borane complex $(Me_2S)(C_6H_5)B(C_5H_4)_2ZrCl_2$ (**1**) was prepared following the literature procedure.¹⁵ Bright yellow **1** crystallizes very readily from hot toluene solution. The green color reported¹⁵ was only observed on exposure of solutions of **1** to air.

The reaction of 1 equiv of LiC_6F_5 with complex **1** was expected to either lead to the borato complex $Li[(C_6F_5)(C_6H_5)B(C_5H_4)_2ZrCl_2]$ or result in alkylation to give $(Me_2S)(C_6H_5)B(C_5H_4)_2Zr(C_6F_5)Cl$. In practice we obtained a mixture of unreacted **1** and a new complex, **2**. The difference in solubility between **1** and **2** made separation straightforward. Elemental analysis indicated that **2** had lost both chloride ligands; this coupled with the presence of a Me_2S donor, a very similar ¹¹B NMR chemical shift to **1**, and ¹⁹F *o*- C_6F_5 resonances consistent with bonding to zirconium led to the identification of the product as $(Me_2S)(C_6H_5)B(C_5H_4)_2Zr(C_6F_5)_2$ (**2**) (Scheme 2). Spectroscopic data of **1** and all new

(12) (a) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489. (b) Pastor, A.; Kiely, A. F.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *528*, 65. (c) Kiely, A. F.; Nelson, C. M.; Pastor, A.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 1324.

(13) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343.

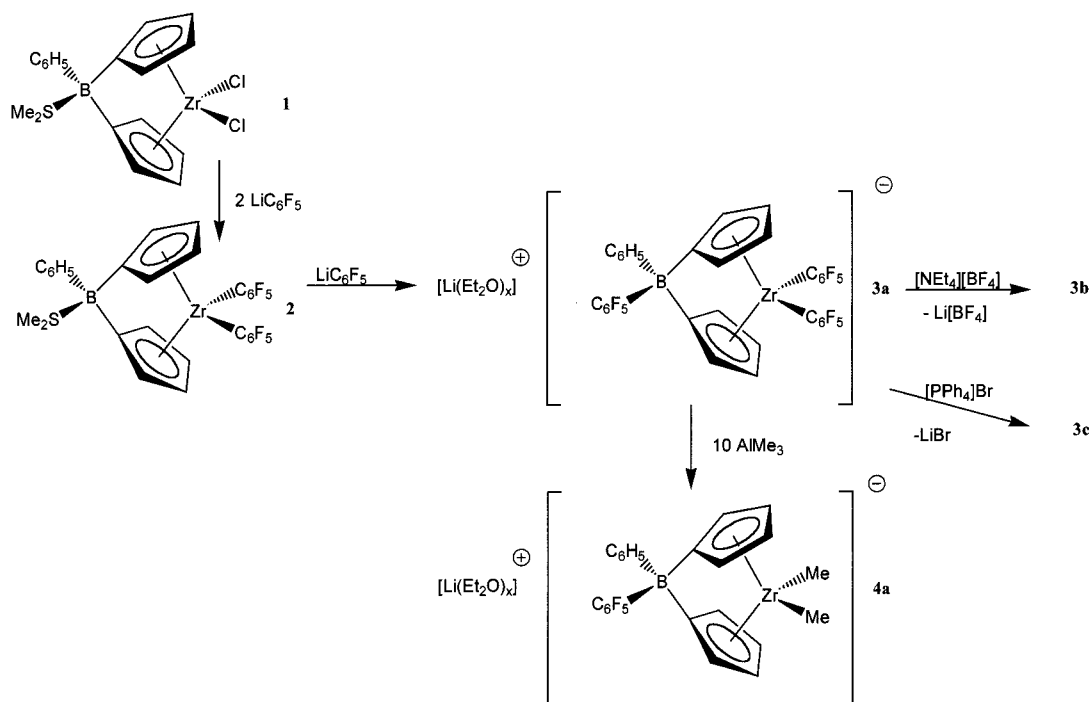
(14) (a) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338. (b) Braunschweig, H.; von Koblinski, C.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 69. (c) Ashe, A. J.; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288.

(15) Stelck, D. S.; Shapiro, P. J.; Basickes, N.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4546.

(16) (a) Rufanov, K. A.; Kotov, V. V.; Kazennova, N. B.; Lemenovskii, D. A.; Avtomonov, E. V.; Lorberth, J. *J. Organomet. Chem.* **1996**, *525*, 287. (b) Rufanov, K. A.; Avtomonov, E. V.; Kazennova, N. B.; Kotov, V. V.; Khvorost, A.; Lemenovskii, D. A.; Lorberth, J. *J. Organomet. Chem.* **1997**, *536–537*, 361. (c) Reetz, M. T.; Wiluhn, M.; Psiorz, C.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1999**, 1105.

(17) Burns, C. T.; Stelck, D. S.; Shapiro, P. J.; Ashwani, V.; Kunz, K.; Kehr, G.; Concolino, T.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5432.

Scheme 2



complexes are collected in Table 1. **2** can be obtained in 70% yield by employing 2 equiv of LiC_6F_5 . Complex **2** was repeatedly observed as a byproduct in crude reaction mixtures with excess LiC_6F_5 . The observation that the first two equivalents of LiC_6F_5 will selectively alkylate at zirconium is in contrast with the literature report stating that clean alkylation first requires exchange of the Me_2S for a more strongly bound PMe_3 donor.¹⁷

The use of a third equivalent of LiC_6F_5 led to displacement of dimethyl sulfide and formation of an *ansa*-borate complex, $[\text{Li}(\text{Et}_2\text{O})_3][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (**3a**). Borate formation is indicated by the low solubility of **3a** in aromatic solvents, the ^{11}B NMR chemical shift ($\delta -11.81$), and the presence of resonances for both $\text{Zr}-\text{C}_6\text{F}_5$ and $\text{B}-\text{C}_6\text{F}_5$ moieties in the ^{19}F NMR spectrum. The presence of two different phenyl substituents on the boron results in four resonances for the cyclopentadienyl protons and two inequivalent $\text{Zr}-\text{C}_6\text{F}_5$ ligands.

The yield of complex **3a** is improved if 4 equiv of LiC_6F_5 are used, presumably because reaction at boron is in competition with the decomposition of the lithium reagent.¹⁸

The cation of complex **3a** can be exchanged readily for $[\text{NEt}_4]^+$ or $[\text{PPh}_4]^+$ to give complexes **3b** and **3c**, respectively (Scheme 2). This leads to small changes in the ^1H NMR spectra of the anion.

Having demonstrated the formation of *ansa*-borate complexes with a $\text{B}-\text{C}_6\text{F}_5$ substituent, we wished to selectively exchange the $\text{Zr}-\text{C}_6\text{F}_5$ ligands for more reactive methyl groups. Efficient zwitterion formation and alkene insertion chemistry would require alkyl exchange since neither C_6F_5 abstraction nor insertion

into a $\text{Zr}-\text{C}_6\text{F}_5$ bond is likely to be facile. Preliminary NMR reactions indicated that the exchange reaction with AlMe_3 did proceed but was slow and led to the formation of side-products. The smoothest reaction, leading to the best characterized zirconium methyl species, was that between the lithium salt **3** and 10 equiv of AlMe_3 carried out over 36 h in dichloromethane. Although the product was not pure, the spectroscopic characterization of the major product was consistent with structure **4** (Scheme 2). The ^{11}B NMR chemical shift ($\delta -10.9$) and observation of a $\text{B}-\text{C}_6\text{F}_5$ group indicate that the borate bridge is intact. As expected, two resonances are observed with ^1H ($\delta 0.14$ and 0.10) and ^{13}C NMR chemical shifts ($\delta 28.92$ and 28.59) that are consistent with $\text{Zr}-\text{Me}$ groups.

A further indication of the ability of aluminum alkyls to exchange with the $\text{Zr}-\text{C}_6\text{F}_5$ groups and produce reactive species is given by ethene polymerization results obtained in the **3b**/MAO system, which show good activities after short induction times (Table 2).

Following the formation of stable *ansa*-borate complexes with one C_6F_5 and one C_6H_5 substituent, we wished to prepare the analogue with two C_6F_5 groups. This compound should have improved stability due to the greater electron-withdrawing capability and steric bulk of the C_6F_5 .

Boron trichloride reacts with 2 equiv of $(\text{SiMe}_3)-(\text{SnMe}_3)\text{C}_5\text{H}_4$ with selective dehalostannylation to yield $\text{BCl}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ (**5**) (Scheme 3). Addition of $\text{ZrCl}_4(\text{Me}_2\text{S})_2$ at 70°C gave $\text{Cl}(\text{Me}_2\text{S})\text{B}(\text{C}_5\text{H}_4)\text{ZrCl}_2$ (**6**), which was purified by recrystallization from dichloromethane. The elemental analysis was consistent with three chlorine atoms per molecule, and the characteristic four resonances were observed for the inequivalent cyclopentadienyl protons. The ^{11}B NMR chemical shift ($\delta 5.0$) indicates a neutral four-coordinate boron atom similar to that observed for the neutral boron bridges with Me_2S donors in **1** and **2**. The ^1H NMR chemical shift of Me_2S

(18) LiC_6F_5 decomposes above ca. -20°C in a potentially explosive reaction to give LiF and benzyne: Chernega, A. N.; Graham, A. J.; Green, M. L. H.; Haggitt, J.; Lloyd, J.; Mehnert, C. P.; Metzler, N.; Souter, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2293. See also ref 3f.

Table 1. ^1H , ^{11}B , ^{13}C , and ^{19}F NMR Data for Complexes 1–10

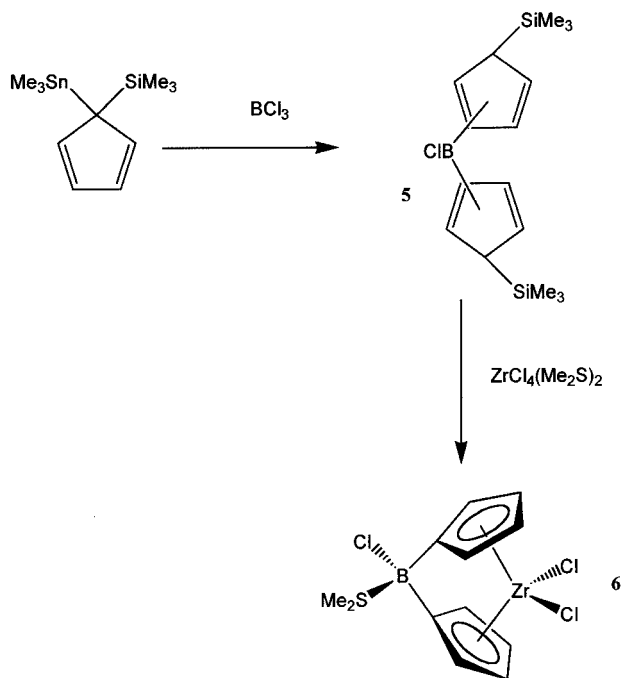
Complex	^{11}B NMR	^1H NMR	assignt	^{13}C NMR	assignt	^{19}F NMR	assignt						
1	2.0	7.73 (d, 2H, $J = 7.8$ Hz) 7.50–7.44 (m, 3H) 6.90 (m, 2H) 6.79 (m, 2H) 5.96 (m, 2H) 5.67 (m, 2H) 2.16 (s, 6H)	<i>o</i> -Ph <i>m,p</i> -Ph C_5H_4 C_5H_4 C_5H_4 C_5H_4 Me_2S	137.83 129.0 128.2 127.2 125.26 125.01 114.9 111.18 18.27	Ph Ph Ph Ph C_5H_4 C_5H_4 C_5H_4 C_5H_4 Me_2S								
	2	-0.6	7.63 (m, 2H) 7.35 (m, 3H) 6.85 (m, 2H) 6.82 (m, 2H) 5.97 (m, 2H) 5.69 (m, 2H) 2.06 (s, 6H)	<i>o</i> -Ph <i>m,p</i> -Ph C_5H_4 C_5H_4 C_5H_4 C_5H_4 Me_2S	135.7 128.7 128.0 120.1 116.5 113.8 18.2	Ph Ph Ph C_5H_4 C_5H_4 C_5H_4 Me_2S	-115.2 (br, 2F) -121.5 (br, 2F) -156.3 (m, 2F) -162.8 (m, 4F)	<i>o</i> -F, C_6F_5 <i>o</i> -F, C_6F_5 <i>p</i> -F, C_6F_5 <i>m</i> -F, C_6F_5					
		3b	-11.81	7.73 (m, 2H) 7.20 (m, 2H) 7.09 (m, 1H) 6.79 (m, 4H) 5.80 (m, 2H) 5.67 (m, 2H)	<i>o</i> -Ph <i>m</i> -Ph <i>p</i> -Ph C_5H_4 C_5H_4 C_5H_4	133.75 127.77 125.2 119.2 118.6 116.5 115.1	<i>o</i> -Ph <i>m</i> -Ph <i>p</i> -Ph C_5H_4 C_5H_4 C_5H_4	-114.4 (br, 2F) -119.1 (br, 2F) -127.21 (d, 2F) -158.3 (tr, 1F) -163.4 (tr, 2F) -163.7 (br, 4F) -165.8 (m, 2F)	<i>o</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>o</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>o</i> -F, $\text{B-C}_6\text{F}_5$ <i>p</i> -F, $\text{B-C}_6\text{F}_5$ <i>p</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>m</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>m</i> -F, $\text{B-C}_6\text{F}_5$				
			4	-10.87	7.87 (m, 2H) 7.26 (m, 2H) 7.11 (tr, 1H) 6.61 (m, 2H) 6.57 (m, 2H) 5.58 (m, 2H) 5.52 (m, 2H) 0.14 (s, 3H) 0.10 (s, 3H)	<i>o</i> -Ph <i>m</i> -Ph <i>p</i> -Ph C_5H_4 C_5H_4 C_5H_4 C_5H_4 Zr-Me Zr-Me	134.34 128.02 125.32 124.92 123.58 115.25 115.12 28.59 28.51	<i>o</i> -Ph <i>m</i> -Ph <i>p</i> -Ph C_5H_4 C_5H_4 C_5H_4 C_5H_4 Zr-Me Zr-Me	-127.87 -160.65 -164.26	<i>o</i> -F, C_6F_5 <i>p</i> -F, C_6F_5 <i>m</i> -F, C_6F_5			
				5	55	7.47 (br, 2H) 6.55 (br, 2H) -0.10 (s, 9H)	C_5H_4 C_5H_4 SiMe_3	149 (br) 132 (br) -1.10	C_5H_4 C_5H_4 SiMe_3				
					6	5	6.85 (m, 2H) 6.79 (m, 2H) 5.96 (m, 2H) 5.72 (m, 2H) 2.61 (s, 6H)	C_5H_4 C_5H_4 C_5H_4 C_5H_4 Me_2S	128.19 125.13 115.68 109.64 18.85	C_5H_4 C_5H_4 C_5H_4 C_5H_4 Me_2S			
						7	14.01	6.96 (m, 2H) 6.84 (m, 2H) 6.04 (m, 2H) 5.73 (m, 2H) 4.82 (q, 4H, $J = 7.2$ Hz) 1.70 (tr, 6H, $J = 7.2$ Hz)	C_5H_4 C_5H_4 C_5H_4 C_5H_4 OCH_2CH_3 OCH_2CH_3	122.0 118.76 117.85 112.06 73.96 15.65	C_5H_4 C_5H_4 C_5H_4 C_5H_4 OCH_2CH_3 OCH_2CH_3	-118.8 (v br, 4F) -155.9 (tr, 1F, $J_{\text{FF}} = 19.5$ Hz) -156.1 (tr, 1F, $J_{\text{FF}} = 19.4$ Hz) -162.6 (br, 4F)	<i>o</i> -F, C_6F_5 <i>p</i> -F, C_6F_5 <i>p</i> -F, C_6F_5 <i>m</i> -F, C_6F_5
8				-1			6.80 (m, 2H) 6.55 (m, 2H) 5.71 (m, 2H) 5.39 (m, 2H)	C_5H_4 C_5H_4 C_5H_4 C_5H_4					
	9a			-12.2			6.91 (m, 4H) 5.78 (m, 4H)	C_5H_4 C_5H_4	119.3 (br) 114.96	C_5H_4 C_5H_4	-118 (br, 4F) -131.96 (d, 4F, $J_{\text{FF}} = 19$ Hz) -157.03 (tr, 2F, $J_{\text{FF}} = 19$ Hz) -158.66 (tr, 2H, $J_{\text{FF}} = 20$ Hz) -162.58 (tr, 4F, $J_{\text{FF}} = 19$ Hz) -163.21 (tr, 2H, $J_{\text{FF}} = 20$ Hz)	<i>o</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>o</i> -F, $\text{B-C}_6\text{F}_5$ <i>p</i> -F, $\text{B-C}_6\text{F}_5$ <i>p</i> -F, $\text{Zr-C}_6\text{F}_5$ <i>m</i> -F, $\text{B-C}_6\text{F}_5$ <i>m</i> -F, $\text{Zr-C}_6\text{F}_5$	
				10a			-12.2	6.76 (tr, 4H, $J = 2.3$ Hz) 5.44 (br, 4H) -0.46 (s, 6H)	C_5H_4 C_5H_4 Zr-Me	118.01 110.48 27.29	C_5H_4 C_5H_4 Zr-Me	-114.85 (d, 4F, $J_{\text{FF}} = 20.85$ Hz) -156.66 (br, 2F) -162.04 (d, 4F, $J_{\text{FF}} = 19$ Hz)	<i>o</i> -F, $\text{B-C}_6\text{F}_5$ <i>p</i> -F, $\text{B-C}_6\text{F}_5$ <i>m</i> -F, $\text{B-C}_6\text{F}_5$

Table 2. Ethene Polymerization Productivities (1 bar)

complex (μmol)	activator (μmol)	AlBu ¹ ₃ (μmol)	temp (°C)	time (s)	polymer yield (g)	productivity ^a
3b (10)	MAO (5000)		20	600	0.466	0.28
3b (10)	MAO (5000)		60	240	0.537	0.80
9a^b (5)	MAO (5000)		20	1200	0.332	0.19
9a (5)	MAO (5000)		60	600	0.560	0.67
9a^c (10)	MAO (6000)		60	600	0.913	1.10
9a (5)	[CPh ₃][B(C ₆ F ₅) ₄] (10)	500	20	180	0.226	0.90
9a (5)	[CPh ₃][B(C ₆ F ₅) ₄] (10)	500	60	180	0.533	2.13
10a (5)	MAO (10000)		20	300	0.095	0.23
10a (5)	MAO (10000)		60	300	0.286	0.69
10a (5)	[CPh ₃][B(C ₆ F ₅) ₄] (5)	500	20	300	0.120	0.29
10a (5)	[CPh ₃][B(C ₆ F ₅) ₄] (5)	500	60	300	0.153	0.37
10b (5)	[CPh ₃][B(C ₆ F ₅) ₄] (10)	500	20	300	0.255	0.61
10b (5)	[CPh ₃][B(C ₆ F ₅) ₄] (10)	500	60	300	0.162	0.39

^a In 10⁶ g PE/(mol M)·h·bar. ^b Ethene uptake rate increases markedly after first 5 min. ^c MAO and **9a** premixed 1 h before polymerization.

Scheme 3



(δ 2.61) is 0.45 ppm downfield of that found for **1**, which indicates greater Lewis acidity at the boron center. Like **1**, complex **6** is soluble in warm toluene and dichloromethane but poorly soluble in light petroleum or diethyl ether.

Using a method similar to that employed for the preparation of **3**, we followed the reaction between **6** and 4 equiv of LiC₆F₅. Again the more reactive site in the molecule was not at boron but at zirconium, and the first step in the reaction sequence was alkylation to form (L)CIB(C₅H₄)₂Zr(C₆F₅)₂ (**7**) (Scheme 4). This compound could be isolated pure by crystallization from diethyl ether. Unlike complex **2**, the alkylation product was the diethyl ether adduct rather than the dimethyl sulfide

adduct, possibly due to reduced steric crowding in the chloro- versus the phenylborane. The identity of **7** was confirmed by elemental analysis, indicating the presence of one chloride ligand; the ¹¹B NMR chemical shift (δ 14.0) and a set of four different cyclopentadienyl proton signals implied two different ligands on boron. The ¹H NMR signals for the coordinated Et₂O show a large downfield shift (δ 4.82 and 1.70). There is no evidence for exchange with free diethyl ether in solution at 20 °C, indicating very strong coordination of the ligand. The ¹⁹F NMR spectrum shows two different Zr–C₆F₅ ligands but no B–C₆F₅ groups. Crude product mixtures from reactions between **6** and up to 6 equiv of LiC₆F₅ invariably contained both **7** and a second new compound, **9a**. The physical properties of **9a** are consistent with formulation as an ionic compound; **9a** is poorly soluble in toluene and can be best purified by precipitating as an oil from a toluene solution by cooling to –30 °C. This oil retains some toluene even when dried under vacuum to an amorphous foam. Unfortunately it proved impossible to crystallize either **9a** or the [NEt₄]⁺ salt, **9b**. Examination of the spectroscopic data (Table 1) provides strong evidence for the formulation of the anion of **9** as [(C₆F₅)₂B(C₅H₄)₂Zr(C₆F₅)₂][–]. The ¹¹B NMR chemical shift at δ –12.2 ppm indicates a four-coordinate anionic borate atom similar to that seen for **3**. Unlike **3**, compound **9** has C_{2v} symmetry, and only two resonances are observed for the cyclopentadienyl protons. The ¹⁹F NMR spectrum (Figure 1) indicates just two types of C₆F₅ group of equal intensity, one with a very broad *o*-F resonance at δ –118 (Zr–C₆F₅) and a sharper signal for *o*-F at δ –132 (B–C₆F₅). The *o*-F signals for the Zr–C₆F₅ group are consistently observed to be broad at room temperature, presumably due to hindered rotation about the Zr–C bond.

The yield of **9a** obtained through reaction of **6** with LiC₆F₅ was found to be highly variable. The use of larger excesses of LiC₆F₅ and longer reaction times did not

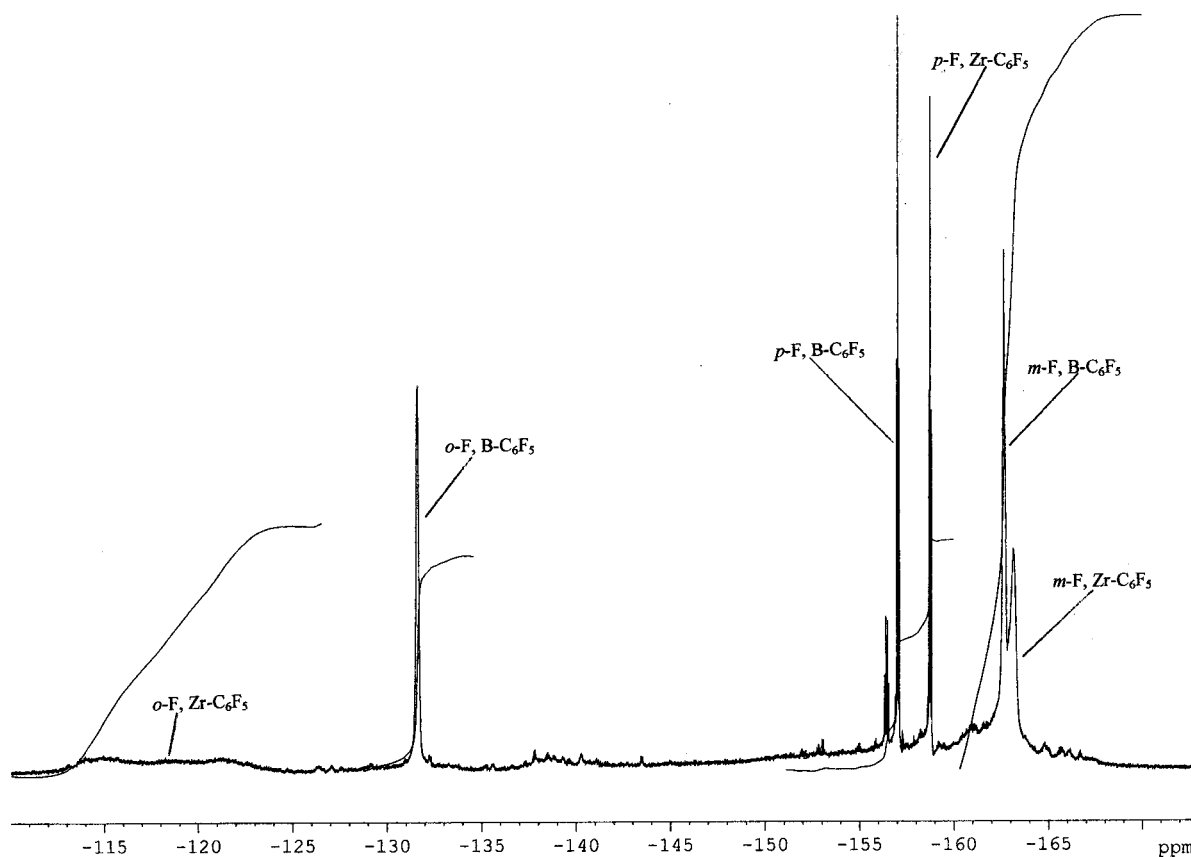
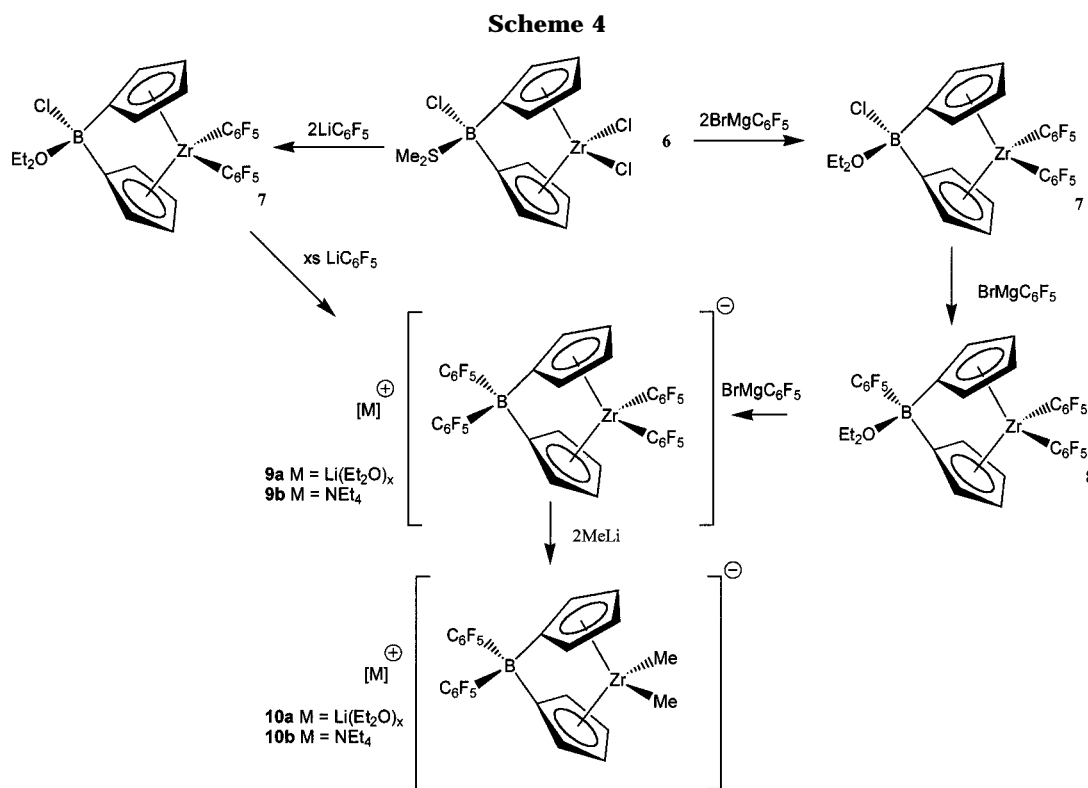


Figure 1. ^{19}F NMR spectrum of **9a**, $[\text{Li}(\text{Et}_2\text{O})_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (282.4 MHz, CDCl_3 , 20 °C).



significantly improve the yield. The instability of the LiC_6F_5 reagent and the low yields for complete conversion to **9a** suggest that LiC_6F_5 decomposition is in competition with arylation at the boron center. Unlike the lithium reagent, $\text{C}_6\text{F}_5\text{MgBr}$ is thermally stable and can be warmed above room temperature without rapid

decomposition. Reactions between 4 equiv of $\text{C}_6\text{F}_5\text{MgBr}$ and **6** (Scheme 4) at room temperature again only lead to compound **7**. However, in small-scale reactions warming to 60 °C leads rapidly to conversion to the anion **9**. On a larger scale reaction times could be as long as 18 h, and it was necessary to monitor progress by ^1H NMR.

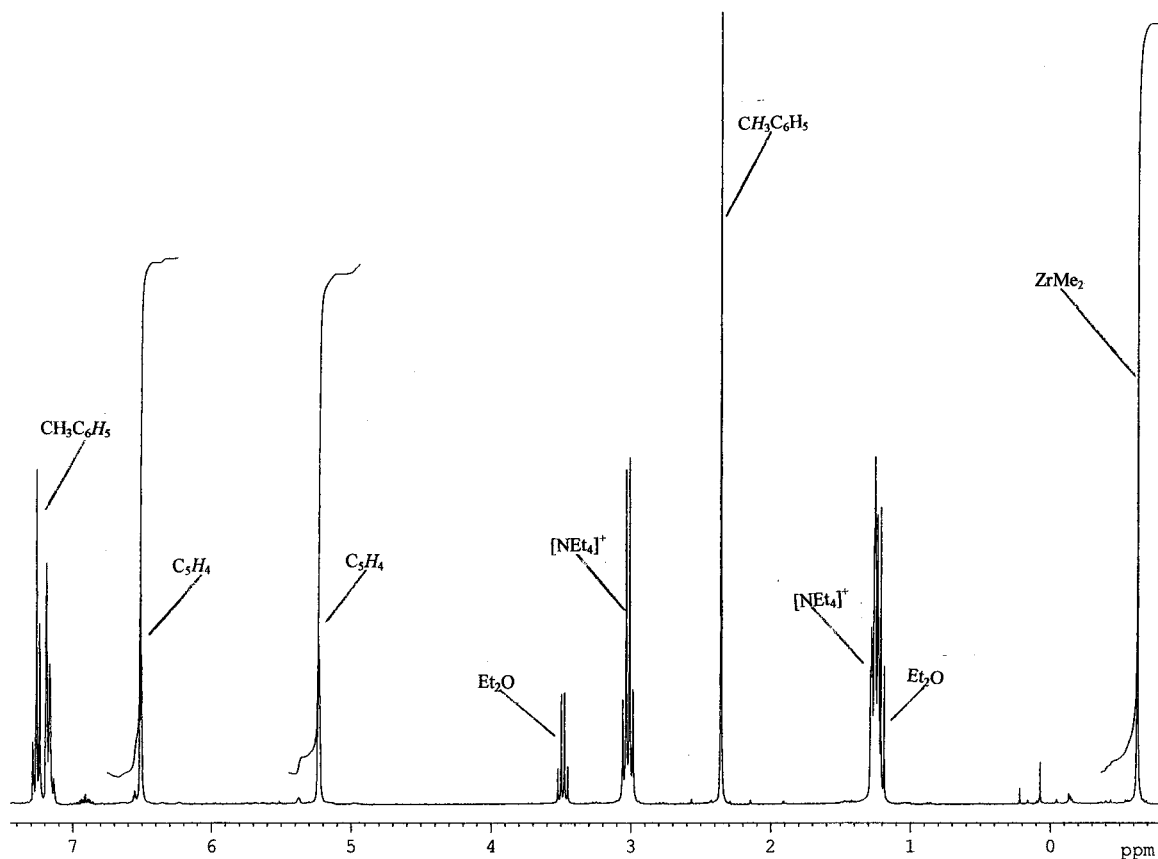


Figure 2. ^1H NMR spectrum of complex **10b**, $[\text{NEt}_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (300.13 MHz, CDCl_3 , 20 °C).

Although at room temperature compound **7** is the only intermediate observed, in reactions that were warmed to 60 °C for prolonged periods, a second intermediate could be identified by ^1H NMR (Scheme 4). Compound **8** could not be isolated, and apart from a new set of four cyclopentadienyl resonances indicating two inequivalent groups bonded to boron and a broad ^{11}B resonance at $\delta -1$ ppm, no other data are available. Compound **8** is tentatively assigned as $(\text{L})(\text{C}_6\text{F}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2$, where L is presumably Et_2O .

Attempts to prepare the dimethyl anion $[(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]^-$ in analogous fashion to **4** were unsatisfactory. The reaction between **9** and AlMe_3 appeared to be very slow indeed, and quantitative conversion to a new complex was not achieved. The reaction between **9** and AlMe_3 will establish equilibrium, and large quantities of AlMe_3 may be required to achieve high conversions.¹⁹

By contrast, the reaction of **9a** with LiMe is exothermic. Spectroscopic investigation of the crude reaction mixture indicated the formation of a new compound, **10a**. Where reactions were attempted on a larger scale, it was thought prudent to add the LiMe at 0 °C and warm slowly to room temperature. When the initial reaction exotherm was avoided, the reaction proceeded much more slowly and a reaction time of 12 h was required for complete alkyl exchange to form **10a**. The $[\text{NEt}_4]^+$ salt **10b** was prepared similarly from **9b**. Compounds **10a** and **10b** were obtained >90% pure by ^1H NMR. However, samples of either **10a** or **10b** pure enough to provide good elemental analysis proved

elusive. Repeated washing, attempted recrystallization, or precipitation steps led only to the growth of new impurity signals, presumably hydrolysis products with very similar solubility properties.

Anion **10** is assigned the structure $[(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]^-$ on the basis of ^1H , ^{11}B , ^{13}C , 2D H–C HETCOR, and ^{19}F NMR spectra. The ^1H NMR spectrum of **10b** is shown in Figure 2. Apart from the cation $[\text{NEt}_4]^+$ and a signal for $[\text{Li}(\text{Et}_2\text{O})_x]^+$, the NMR spectrum is very simple, consisting of two pseudo-triplets for the AA'BB' pattern of a substituted cyclopentadienyl ligand, broadened by proximity to the quadrupolar boron nucleus, and a sharp CH_3 singlet at $\delta -0.6$. The identity of this singlet as the Zr–Me resonance was confirmed by the observation of coupling to a ^{13}C NMR signal at $\delta 23.56$ ppm. The ^{11}B NMR chemical shift is the same as that observed for **9**. The ^{19}F NMR indicates just one type of C_6F_5 group, as expected, but although sharp, the *o*-F resonance for the B– C_6F_5 group is observed to be downfield shifted at $\delta -114.85$ ppm; the reason for this is not clear.

Ethene Polymerizations. The ionic complexes **3b**, **9a**, **10a**, and **10b** were employed as precatalysts for ethene polymerization, and the results are presented in Table 2. The productivity observed for **3b** is similar to that observed for Shapiro's *ansa*-borates $[\text{PPN}][(\text{Cl})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2]$ (0.57×10^6 g PE mol $^{-1}$ h $^{-1}$ bar $^{-1}$) and $[\text{Cp}^*_2\text{Al}][(\text{Me})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2]$ (0.9×10^6 g PE mol $^{-1}$ h $^{-1}$ bar $^{-1}$).¹⁷ The productivity for **9a** activated with MAO is comparable. Somewhat higher productivities are obtained if the catalyst is premixed with MAO, which is consistent with slow generation of the active species. For simple zirconocenes productivity is highly

(19) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

dependent on the mode of activation.^{5d} The activation of **9a** with $\text{AlBu}^i_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ gives a productivity of 2.13×10^6 g PE mol⁻¹ h⁻¹ bar⁻¹ at 60 °C. However, the use of the dimethyl complex **10a** does not lead to an increase in productivity over **9a** under these polymerization conditions. Polymerizations with **10b** indicate that in the presence of an excess of aluminum reagent the nature of the precatalyst counteranion and any associated diethyl ether does not have a dramatic impact on productivity.

Conclusions

The chloro borane bridged *ansa*-zirconocene $\text{Cl}(\text{Me}_2\text{S})\text{B}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ is accessible through the dehalosilylation reaction of $\text{BCl}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ with $\text{ZrCl}_4(\text{Me}_2\text{S})_2$. The reaction of this complex and the phenyl analogue $(\text{Me}_2\text{S})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ with 2 equiv of LiC_6F_5 leads to selective arylation to form neutral bis(pentafluorophenyl)zirconium compounds. The use of 5 equiv of LiC_6F_5 leads to attack at boron, affording anionic borates. The $\text{Zr}-\text{C}_6\text{F}_5$ groups are exchanged for $\text{Zr}-\text{Me}$ through reaction with AlMe_3 or LiMe to give $[\text{Li}(\text{Et}_2\text{O})_x][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ and $[\text{Li}(\text{Et}_2\text{O})_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$, respectively. These anionic *ansa*-zirconocenes can be activated with MAO or $\text{AlBu}^i_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ to give ethene polymerization catalysts.

Experimental Section

General Considerations. All manipulations were performed under a dinitrogen atmosphere using Schlenk techniques. Solvents were distilled under N_2 over sodium (toluene), Na/K alloy (diethyl ether, light petroleum (bp 40–60 °C)), or CaH_2 (dichloromethane). NMR solvents were dried over 4 Å molecular sieves (C_6D_6 , CD_2Cl_2 , CDCl_3). NMR spectra were recorded on a Bruker DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C NMR) or external $\text{BF}_3 \cdot \text{OEt}_2$ (¹¹B) and CFCl_3 (¹⁹F). Ethene polymerizations (1 bar) were performed as described.^{5d} $\{(\text{Me}_2\text{S})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\}\text{ZrCl}_2$ was prepared according to a literature procedure.¹⁵

Preparation of $\{(\text{Me}_2\text{S})(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\}\text{Zr}(\text{C}_6\text{F}_5)_2$ (2**).** To a solution of 0.94 g (3.8 mmol) of $\text{C}_6\text{F}_5\text{Br}$ in light petroleum, held at -78 °C, was added slowly 2.4 mL of a 1.6 M solution of *n*-BuLi (3.8 mmol). The reaction mixture was stirred for 1 h at -78 °C before 1.87 g (1.9 mmol) of solid **1** was added. The reaction mixture was stirred for 2 h before warming to room temperature. A yellow solution formed above a pale solid. The solid was allowed to settle and the solution filtered off. The solvent was taken off under reduced pressure, leaving a yellow foam. Extraction with cold (-30 °C) toluene and removal of the toluene under vacuum gave **2** as a yellow solid. ¹H NMR indicated that **2** retained 0.5 equiv of toluene. The yield of **2** was 1.0 g (1.3 mmol, 70%). Anal. Calcd for $\text{C}_{30}\text{H}_{19}\text{BF}_{10}\text{SZr} \cdot 0.5\text{C}_7\text{H}_8$: C, 53.68; H, 3.09. Found: C, 53.85; H, 3.08.

Preparation of $[\text{Li}(\text{Et}_2\text{O})_x][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (3a**).** To 6 mmol of LiC_6F_5 in 60 mL of diethyl ether at -78 °C was added 1.25 g (2 mmol) of **1** and the mixture stirred for 1 h and allowed to warm very slowly. At ca. -60 °C all the solid **1** had dissolved, leaving only a very small amount of white solid. By ca. -50 °C a thick precipitate had formed. As the suspension was warmed further, the solid dissolved, leaving only a small amount of insoluble material after stirring overnight. The solids were separated by filtration, and the solvent was taken off under reduced pressure to give a yellow foam. Crude NMR analysis indicated a mixture of **2** and a new complex, **3a**. Washing with toluene to remove **2** gave **3a**, yield 1.3 g (1.35 mmol, 67%).

Preparation of $[\text{Et}_4\text{N}][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (3b**).** To 4 mmol of crude **3a** was added 0.84 g (4 mmol) of $[\text{Et}_4\text{N}]\text{Br}$, followed by 30 mL of dichloromethane. The reaction mixture was then stirred for 1 h. The solids were allowed to settle and separated by filtration. Removal of the solvent yielded a yellow-brown foam, 3.2 g (3.4 mmol, 85%). Repeated attempts to recrystallize from a range of solvents were unsuccessful. Anal. Calcd: C, 54.36; H, 3.58; N, 1.51. Found: C, 54.05; H, 3.6; N, 1.35.

Preparation of $[\text{PPh}_4][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (3c**).** Following a procedure similar to that for **3b**, 1.40 g (1.45 mmol) of **3a** and 0.78 g (1.87 mmol) of $[\text{PPh}_4]\text{Br}$ were reacted in 20 mL of dichloromethane. Removal of excess PPh_4Br and solvent left a dark yellow foam, yield 1.5 g (1.30 mmol, 90%). Repeated attempts at recrystallization were unsuccessful.

Preparation of $[\text{Li}(\text{Et}_2\text{O})_x][(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (4**).** To a solution of 10 mL of AlMe_3 (1 M, 10 mmol) in dichloromethane was added 0.75 g of **3a** (0.84 mmol) and the reaction mixture stirred. There was an initial vigorous reaction. The reaction mixture was allowed to stand for 36 h. Light petroleum was added to precipitate the product, and the solvents were filtered off before drying in vacuo to give crude **4** as a tan-colored foam.

Preparation of $\text{ClB}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ (5**).** To a solution of 15 mmol of BCl_3 dissolved in 150 mL of toluene was added 9.03 g (30 mmol) of $\text{C}_5\text{H}_4(\text{SiMe}_3)(\text{SnMe}_3)$. The reaction mixture was heated to reflux for 5 h, during which time the solution darkened slightly in color. Removal of the volatiles at 0.1 mmHg, 50 °C, yielded a yellow-orange oil, which crystallized very slowly when stored at 5 °C. The ¹H NMR spectrum indicated that the yield was essentially quantitative. The compound was used without further purification.

Preparation of $(\text{Me}_2\text{S})\text{ClB}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (6**).** **5** (15 mmol) was dissolved in 100 mL of toluene, and 5.4 g (15 mmol) of $\text{ZrCl}_4(\text{Me}_2\text{S})_2$ was added. The reaction mixture was warmed to 70 °C and stirred overnight. The solution gradually darkened to orange-brown, and a small amount of dark brown solid precipitated. The toluene was removed under vacuum and the product extracted with dichloromethane. The solution was concentrated until crystals persisted and cooled to -25 °C overnight, giving a mass of pale yellow crystals. Yield (two fractions): 4 g (10 mmol, 66%). ¹H NMR spectra of samples of **6** indicate the presence of between 0.1 and 0.2 equiv of toluene, which is only very slowly lost under vacuum. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{BCl}_3\text{SZr} \cdot 0.15(\text{C}_7\text{H}_8)$: C, 38.00; H, 3.71; Cl, 25.78. Found: C, 38.00; H, 3.47; Cl, 26.60.

Preparation of $[(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2][\text{Li}(\text{Et}_2\text{O})_4]$ (9a**).** To a solution of 27.2 mmol of LiC_6F_5 in 100 mL of Et_2O at -78 °C was added **6** (2.17 g, 5.44 mmol). The reaction mixture was allowed to warm very slowly to room temperature over a period of 6 h. Removal of the volatiles in vacuo, extracting with 60 mL of toluene, and cooling to -25 °C precipitated **9a** as brown oil, yield 1.84 g (1.53 mmol, 28%).

Isolation of $(\text{Et}_2\text{O})\text{ClB}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (7**).** Otherwise following the procedure described for **9a**, the reaction mixture was warmed to room temperature, and the solids were separated by filtration. The diethyl ether solution was cooled to -25 °C overnight, and the resulting pale yellow crystals of **7** were isolated and dried under vacuum. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{BClF}_{10}\text{OZr} \cdot 0.66\text{C}_4\text{H}_{10}\text{O}$: C, 47.59; H, 3.43; Cl, 4.90. Found: C, 47.74; H, 3.43; Cl, 5.72.

Preparation of $[\text{Et}_4\text{N}][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2]$ (9b**).** A solution of 80 mmol of $\text{C}_6\text{F}_5\text{MgBr}$ in 200 mL of Et_2O was added via a cannula to a cold (0 °C) solution of 6.4 g (16 mmol) of **6** dissolved in 200 mL of toluene. The brown reaction mixture was allowed to warm to room temperature, and ca. 150 mL of Et_2O was removed under reduced pressure. The solution was then warmed to 60 °C and the reaction monitored by ¹H NMR. After 18 h the toluene was stripped off under vacuum. Solid $[\text{Et}_4\text{N}]\text{Br}$, 3.36 g (16 mmol), was added, followed by 200 mL of CH_2Cl_2 . The mixture was stirred for 1 h before 100 mL of

petroleum ether was added to assist with solid settling and filtration. The solvents were removed to give a sticky brown solid which still contained some CDCl_3 -insoluble material as well as a quantity of $(\text{C}_6\text{F}_5)\text{B}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{C}_6\text{F}_5)_2\cdot\text{OEt}_2$ (**8**). The solid was washed with petroleum ether to remove **8** and re-extracted with toluene. Removal of the toluene gave compound **9b** as a pale brown foam, yield 6.58 g (6.4 mmol, 40%). The NMR data are very similar to those of **9a**.

Preparation of $[\text{Li}(\text{Et}_2\text{O})_4][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (10a**).** To a solution of 3.2 g (2.66 mmol) of **9a** in 60 mL of diethyl ether was added 3.4 mL of 1.6 M LiMe (5.4 mmol). The solution began to reflux. After stirring for a further 2 h, the mixture was filtered to remove a dark insoluble precipitate and taken to dryness. The ^1H NMR spectrum of the crude product was consistent with the formation of **10a**. Extraction with toluene and precipitation with light petroleum produced an oil, which was thoroughly dried under vacuum to give a sticky yellow solid, yield 1.45 g (1.62 mmol, 30%).

Preparation of $[\text{Et}_4\text{N}][(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_5\text{H}_4)_2\text{ZrMe}_2]$ (10b**).** To a suspension of 5.3 g (5.1 mmol) of **9b** in 100 mL of diethyl ether was added 6.4 mL of 1.6 M LiMe. The reaction was monitored by ^1H NMR and after 4 h at room temperature

appeared to be complete. The solution was filtered and separated from a dark insoluble material and the ether removed under reduced pressure. The product was then separated from metal halides by extraction with dichloromethane. Removal of the dichloromethane and characterization by ^1H NMR indicated the presence of impurities, particularly the presence of diethyl ether. A second extraction with toluene produced a pale yellow solution, which was filtered. Removal of the toluene and thorough drying under vacuum yielded **10b**. NMR signals due to Et_2O persisted even after prolonged drying, suggesting the presence of a small amount of $[\text{Li}(\text{Et}_2\text{O})_n]^+$ cation.

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Supporting Information Available: For compounds for which analyses are not reported, copies of their NMR spectra are available. This material can be obtained free of charge via the Internet at <http://pubs.acs.org>.

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