Novel *ansa*-Metallocenes with a Single Boron Atom in the Bridge: Syntheses, Reactivities, and X-ray Structures of $\{Ph(L)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (L = SMe_2, PMe_3)

Daniel S. Stelck, Pamela J. Shapiro,* and Naomi Basickes

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

Arnold L. Rheingold

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received March 25, 1997[⊗]

The syntheses and X-ray crystal structures of the boron-bridged *ansa*-metallocene complexes $[\{Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]\cdot C_6D_6$ (**2**) and $[\{Ph(Me_3P)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (**3**) are reported. Complex **2** is obtained as the product of a double dehalodesilylation reaction between $PhB(C_5H_4SiMe_3)_2$ and $ZrCl_4(SMe_2)_2$. The dimethyl sulfide adduct of **2** is readily replaced with trimethylphosphine to afford **3**. Efforts to alkylate **2** were unsuccessful, presumably due to the lability of the dimethyl sulfide and, hence, its inability to protect the boron bridge from nucleophilic attack by alkyl anions. In contrast, the trimethylphosphine adduct in **3** binds tightly enough to the boron bridge to protect it from nucleophilic attack. Also, unlike **2**, complex **3** is activated by methylalumoxane toward the polymerization of ethylene.

Introduction

Over the past decade, *ansa*-metallocene complexes of the early transition metals, particularly the group 4 metals, have played a prominent role in homogeneous catalysis,[1,2] especially in Ziegler-Natta-type olefin polymerization.[3−5] Carbon[6−15] and silicon[6,16−25] are the most commonly used elements in the bridge, although early-transition-metal *ansa*-metallocenes with Ge,[17,18] Sn,[26] P,[27] and As[28] bridges have been prepared. The incorporation of a small Lewis acidic atom in the bridge would present a number of interesting ramifications to the chemistry of *ansa*-metallocenes. The Lewis-acidic bridge could offer new catalytic pathways to these complexes by participating intramolecularly in their reaction chemistry.[29] Even more tantalizing is the possibility of employing the Lewis acid as a flexible arm for controlling the geometry, and hence the reactivity, of *ansa*-metallocenes through its ability to reversibly coordinate Lewis bases.

With these goals in mind, we have designed the boron-bridged dicyclopentadienyl ligand precursor $PhB(C_5H_4SiMe_3)_2$ (**1**),[30] which we have used to prepare the *ansa*-zirconocene complex $\{Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (**2**). The solid-state structure of **2** has been determined and is described herein along with our efforts to alkylate the zirconium. The dimethyl sulfide adduct on the boron is labile, as evidenced by the dynamic ^1H NMR spectra of **2** in solution and the facile substitution of the adduct with more tightly binding trimethylphosphine to form $\{Ph(Me_3P)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (**3**). Whereas the dimethyl sulfide adduct of **2** does not protect the boron bridge adequately from nucleophilic attack by the alkyl anions intended for the zirconium center, the phosphine adduct in **3** binds tightly enough to allow alkylation of the zirconium. Thus, the synthesis of dialkyl derivatives

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

[1] Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262−1284.

[2] Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965−994.

[3] Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

[4] Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270.

[5] Thayer, A. M. *Chem. Eng. News* **1995**, *73*, 15−20.

[6] Burger, P.; Hortmann, K.; Diebold, J.; Brintzinger, H.-H. *J. Organomet. Chem.* **1991**, *417*, 9−27.

[7] Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H.-H. *Organometallics* **1992**, *11*, 1319−1327.

[8] Dorer, B.; Prosenc, M.-H.; Rief, U.; Brintzinger, H. H. *Organometallics* **1994**, *13*, 3868−3872.

[9] Erker, G.; Wilker, S.; Krüger, C.; Nolte, M. *Organometallics* **1993**, *12*, 2140−2151.

[10] Nifant'ev, I. E.; Churackov, A. V.; Urazowski, I. F.; Mkoyan, S. G.; Atovmyan, L. O. *J. Organomet. Chem.* **1992**, *435*, 37−42.

[11] Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1979**, *173*, 175−185.

[12] Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 69−77.

[13] Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1970**, *28*, 2497−2499.

[14] Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79−90.

[15] Halterman, R. L.; Ramsey, T. M.; Pailes, N. A.; Khan, M. A. *J. Organomet. Chem.* **1995**, *497*, 43−53.

[16] Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171−180.

[17] Klouras, N. *Monatsh. Chem.* **1981**, *112*, 887−897.

[18] Köpf, H.; Kahl, W. *J. Organomet. Chem.* **1974**, *64*, C37−C40.

[19] Luttikhedde, H. J. G.; Leino, R. P.; Näsman, J. H.; Ahlgrén, M.; Pakkanen, T. *J. Organomet. Chem.* **1995**, *486*, 193−198.

[20] Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H.-H. *J. Organomet. Chem.* **1993**, *12*, 1931−1935.

[21] Mitchell, J. P.; Hajela, S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045−1053.

[22] Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. *Organometallics* **1994**, *13*, 954−963.

[23] Mansel, S.; Rief, U.; Prosenc, M.-H.; Kirsten, R.; Brintzinger, H.-H. *J. Organomet. Chem.* **1996**, *512*, 225−236.

[24] Barsties, E.; Schaible, S.; Prosenc, M.-H.; Rief, U.; Röll, W.; Weyand, O.; Dorer, B.; Brintzinger, H.-H. *J. Organomet. Chem.* **1996**, *520*, 63−68.

[25] Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347−1349.

[26] Herrmann, W. A.; Morawietz, M. J. A.; Herrmann, H.-F.; Küber, F. *J. Organomet. Chem.* **1996**, *509*, 115−117.

[27] Köpf, H.; Klouras, N. *Monatsh. Chem.* **1983**, *114*, 243−247.

[28] Klouras, N. *Z. Naturforsch.* **1991**, *46B*, 647−649.

[29] Klang, J. A.; Collum, D. B. *Organometallics* **1988**, *7*, 1532−1537.

[30] Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2393−2398.

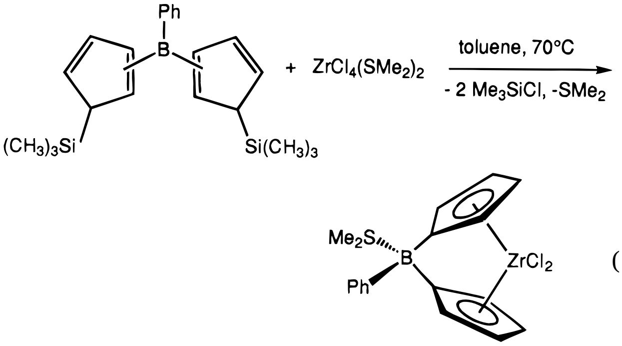
S0276-7333(97)00253-7 CCC: $14.00

of **3** and the activation of **3** toward ethylene polymerization by methylalumoxane have been demonstrated.

During the preparation of this paper, a report by Rufanov *et al.* appeared describing the synthesis of a base-free form of this *ansa*-zirconocene complex by a closely related route;[42] however, neither a molecular weight determination nor an X-ray structure was reported to confirm a mononuclear, *ansa*-type geometry for the complex. Our repeated attempts to reproduce the synthesis of the base-free complex as described by these authors have yielded impure materials which exhibit none of the ^{1}H NMR spectral features of the compound they reported. We are currently exploring alternate synthetic approaches to this purported base-free, boron-bridged *ansa*-zirconocene complex.

Results and Discussion

Synthesis and X-ray Crystal Structure of the *ansa*-Zirconocene Complex. Our synthetic approach to **2** employs the dicyclopentadienylborane ligand PhB-$(C_5H_4SiMe_3)_2$ (**1**) which reacts with an equivalent amount of $ZrCl_4(SMe_2)_2$[31] to afford the dimethyl sulfide adduct of the *ansa*-metallocene complex (eq 1). Even when 2 equiv of zirconium reagent is used in the reaction, complex **2** is formed preferentially and is the only species isolated cleanly from the reaction. This contrasts with the corresponding reaction between **1** and $TiCl_4$, which affords only the bimetallic complex $[TiCl_3\{\eta^5\text{-}C_5H_4\}]_2BPh$.[30] Interestingly, compound **1** does not react with $ZrCl_4$, $ZrCl_4(thf)_2$, or $ZrCl_4(tht)_2$ (thf = tetrahydrofuran; tht = tetrahydrothiophene) in toluene, tetrahydrofuran, or methylene chloride, even at elevated temperatures.[32] Apparently, the boryl substituent on the cyclopentadienyl ring renders the silyl group less labile toward substitution, such that the reaction proceeds only when the zirconium chloride is solvated by weakly coordinating dimethyl sulfide ligands.



(1)

An ORTEP drawing of the molecular structure of **2**, determined as a benzene solvate, is shown in Figure 1. Crystallographic data and selected bond lengths and bond angles are listed in Tables 1 and 2, respectively. Noteworthy is the C(1)−B−C(1A) angle of 101.1(2)°. This bridge angle is wider than the 99° angle encountered in carbon-bridged *ansa*-zirconocene complexes[10,33] and is substantially wider than the angles of 92.4−95.5° measured for silicon-bridged *ansa*-zirconocene complexes.[16,19,23−25] Accordingly, the cent−Zr−cent angle (cent = Cp centroid), at 121.3(1)°, is quite narrow in comparison to the other single-atom-bridged complexes, and the 65.9° dihedral angle between the cyclopentadienyl ring planes is rather wide.[20,34] Large, bridge-induced distortions from the geometries of normal, unbridged bent-sandwich complexes can have a dramatic influence on the reactivity of metallocenes.[20,35−39]

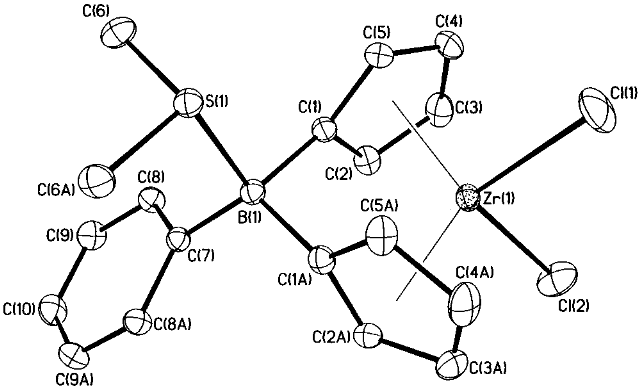


Figure 1. ORTEP drawing of $[\{Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]\cdot C_6D_6$. Thermal ellipsoids are plotted at 50% probability.

Table 1. Crystallographic Data for $\{Ph(L)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (2, L = SMe_2; 3, L = PMe_3)

	2 (L = SMe_2)	**3** (L = PMe_3)
formula	$C_{18}H_{19}BCl_2SZr\cdot C_6D_6$	$C_{19}H_{22}BCl_2PZr$
fw	518.43	454.27
cryst syst	orthorhombic	orthorhombic
space group	*Pnma*	*Pbca*
a (Å)	24.4990(2)	14.6333(2)
b (Å)	9.48930(10)	11.9996(2)
c (Å)	10.06690(10)	22.8114(2)
V (Å$^{3)}$	2340.34(3)	4005.54(9)
Z	4	8
D_{exptl} (g cm^{-3})	1.471	1.395
μ(Mo Kα) (cm^{-1})	8.12	8.94
T (K)	218	173
no. of rflns (collctd, indpdnt)	8602, 2664	13683, 4459
$R(F)$, $R_w(F^2)$,[a] %	2.43, 7.11	5.03, 10.64

[a] $R(F) = \sum | |F_o| - |F_c| |/\sum |F_o|$; $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/[\sum w(F_o)^2]]^{1/2}$.

Table 2. Selected Bond Distances and Angles for $\{Ph(L)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (2, L = SMe_2; 3, L = PMe_3)

(**2**, L = SMe_2)		(**3**, L = PMe_3)	
	(a) Bond Distances (Å)		
Zr(1)−Cent	2.190(1)	Zr(1)−Cent(11−15)	2.208(4)
		Zr(1)−Cent(16−20)	2.201(4)
Zr(1)−Cl(1)	2.4408(7)	Zr(1)−Cl(1)	2.4532(12)
Zr(1)−Cl(2)	2.4411(6)	Zr(1)−Cl(2)	2.4609(11)
B(1)−S(1)	2.009(2)	B(1)−P(1)	1.988(4)
B(1)−C(1)	1.618(2)	B(1)−C(11)	1.645(5)
B(1)−C(7)	1.598(3)	B(1)−C(16)	1.640(5)
		B(1)−C(25)	1.625(5)
	(b) Bond Angles (deg)		
Cent−Zr(1)−Cent	121.3(2)	Cent−Zr(1)−Cent	121.1(6)
Cl(1)−Zr(1)−Cl(2)	99.66(3)	Cl(1)Zr(1)−Cl(2)	99.22(5)
C(1)−B(1)−C(1a)	101.1(2)	C(11)−B(1)−C(16)	100.1(3)
S(1)−B(1)−C(7)	109.22(14)	P(1)−B(1)−C(25)	103.5(2)

---

(31) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426−2427.

(32) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210−214.

(33) Green, M. L. H.; Ishihara, N. *J. Chem. Soc., Dalton Trans.* **1994**, 657−665.

(34) Huttenloch, M. E.; Diebold, J.; Rief, U.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 3600−3607.

(35) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575.

(36) Piers, W. E.; Shapiro, P. J.; Bercaw, J. E. *Synlett* **1990**, *2*, 74−84.

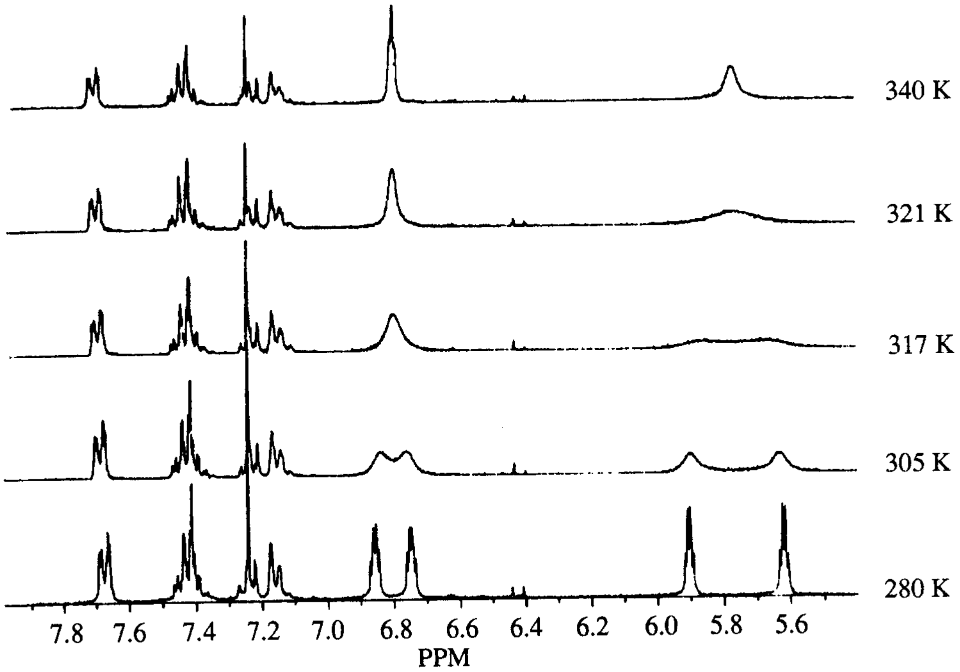


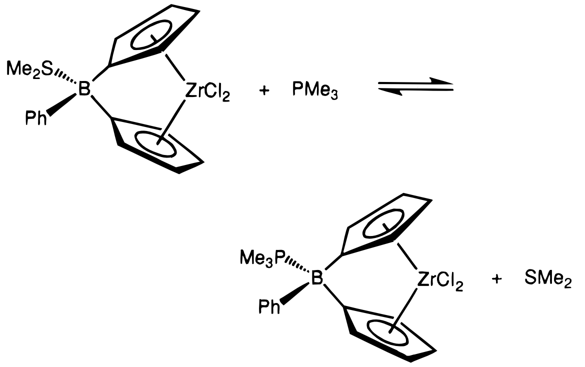
Figure 2. Variable-temperature ^{1}H NMR spectra of [{Ph(Me$_2$S)B(η^5-C$_5$H$_4$)$_2$}ZrCl$_2$] illustrating the coalescence of diastereotopic hydrogen atoms on the cyclopentadienyl rings.

In the absence of a Lewis base adduct to make the bridging boron atom four-coordinate, an even wider angle would exist between the boron and the ring carbons. For example, the 127° bridge angle determined for the base-free, boron-bridged bimetallic complex [TiCl$_3${η^5-C$_5$H$_4$}]$_2$BPh),[30] while not directly comparable to an *ansa*-metallocene bridge angle, illustrates the dramatic widening of the bridge that can result from rehybridization of the boron atom from sp^3 to sp^2.

Such a large bridge angle would be expected to produce a highly strained *ansa*-metallocene complex. Nevertheless, our variable-temperature ^{1}H NMR experiments revealed that the dimethyl sulfide can be labilized from the boron to epimerize the prochiral boron center, as evidenced by the site exchange of the two pairs of diastereotopic cyclopentadienyl ring protons (Figure 2). The exchange rate was calculated as k = 2.6 × 10^{-2} s^{-1} from the coalescence of the cyclopentadienyl proton resonances at δ 5.6 and 5.9 in the "frozen-out" spectrum (280 K). This corresponds to a $\Delta G^‡$ value of 21 kcal/mol for labilization of the dimethyl sulfide adduct from the boron. The presence of excess dimethyl sulfide did not affect the coalescence behavior of the sample, thus ruling out the involvement of a bimolecular process in the epimerization of the boron bridge.

Other structural features of the zirconocene fragment are unremarkable. The Zr–Cl bond lengths of 2.4408(7) and 2.4411(6) Å are comparable to those in other *ansa*-zirconocene dichloride complexes.[6,8,20,40] The Cl(1)–Zr–Cl(2) angle of 99.66(3)° is also normal. The distances between the boron atom and C(1) of the cyclopentadienyl rings and C(7) of the phenyl ring, at 1.618(2) and 1.598(3) Å, respectively, are slightly longer than the corresponding distances in the bimetallic complex [TiCl$_3${η^5-C$_5$H$_4$}]$_2$BPh.[30] This lengthening can be attributed to the increased p character in the bonds of the four-coordinate boron. The boron–sulfur distance of 2.009(2) Å is longer than the sum of their covalent radii (1.92 Å),[41] as one would expect for a weaker, dative interaction between the two atoms.

The dimethyl sulfide adduct is readily replaced with trimethylphosphine to form {Ph(Me$_3$P)B(η^5-C$_5$H$_4$)$_2$}-ZrCl$_2$ (**3**) (eq 2). Unlike dimethyl sulfide, the trimethylphosphine adduct is nonlabile on the NMR time scale. No change in the ^{1}H NMR spectrum of **3** in CDCl$_3$ was observed upon heating the sample up to 340 K. The high affinity of boron toward trimethylphosphine has been demonstrated previously.[42] In fact, BH$_3$ has been used as a protecting group for the phosphorus in alkylphosphine synthesis.[43] As will be described below, the phosphine can also serve as a protecting group for



(2)

---

[37] Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159–167.

[38] Schwemlein, H.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *256*, 285–289.

[39] Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395–402.

[40] Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *369*, 343–357.

[41] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4 ed.; Harper Collins: New York, 1993; p 292.

[42] Odom, J. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, pp 298–301.

[43] Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317–4325.

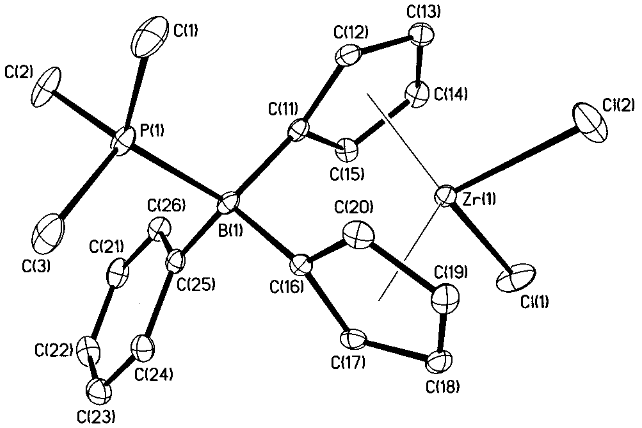


Figure 3. ORTEP drawing of [{Ph(Me$_3$P)B(η^5-C$_5$H$_4$)$_2$}-ZrCl$_2$]. Thermal ellipsoids are plotted at 50% probability.

the boron by blocking it from nucleophilic attack by alkyl anions.

An X-ray crystal structure of **3** was obtained in order to determine if changing the Lewis base adduct from SMe$_2$ to PMe$_3$ has any noticeable effect on the overall geometry of the metallocene. An ORTEP drawing of the molecule is shown in Figure 3. As can be seen from the data in Table 2, the only significant change in the geometry of the complex that resulted from this particular Lewis base substitution is the P−B−C(25) angle (103.5(2)°), which is considerably narrower than the more tetrahedral-like S−B−C(7) angle (109.22(14)°) exhibited by **2**. The narrower bond angle reflects increased p character in the boron orbitals involved in bonding to the phosphine and the phenyl ring. This increased p character, by making the boron s−p hybrid more directional and more diffuse, should allow greater overlap between the boron and the phosphorus. The B−P distance of 1.988(4) Å is shorter than the B−S distance in **2** despite the larger covalent radius of phosphorus relative to sulfur. Furthermore, B-C(11), B−C(16), and B−C(25) are slightly longer than the corresponding bonds in **2**. All of these features reflect the greater affinity of the boron bridge for the trimethylphosphine.

Alkylation of the *ansa*-Zirconocene Complexes. Substitution of the chloride atoms on the zirconium with more reactive σ-bonding ligands is desirable for exploring the fundamental reactivity of this system and determining its potential application toward catalysis. Attempts to alkylate **2** using LiMe, LiCH(SiMe$_3$)$_2$, and ZnMe$_2$ resulted in decomposition. On the basis of earlier results with the borylcyclopentadienyltitanium system,[30] we attribute this decomposition to the vulnerability of the boron to nucleophilic attack by the alkyl anions. When we tried to prealkylate ZrCl$_4$(SMe$_2$) with Me$_2$Zn *in situ* prior to introducing **1**, the only product that was isolated cleanly from the reaction was (Me$_3$SiC$_5$H$_4$)ZrCl$_3$(SMe$_2$) (Experimental Section), indicating that the boron bridge had been cleaved.

In contrast, the trimethylphosphine adduct **3** has been successfully alkylated by LiR (R = CH$_2$SiMe$_3$, Me) and MgRCl (R = CH$_2$C$_6$H$_5$) to form the corresponding {Ph(Me$_3$P)B(η^5-C$_5$H$_4$)$_2$}ZrR$_2$ complexes. A full description of the synthesis and characterization of these alkyl derivatives will be provided in a forthcoming publication.[44] Further chemistry involving these *ansa*-zirconocene complexes, particularly their application toward olefin polymerization chemistry, is currently being explored. We have found that complex **3**, but not complex **2**, is activated toward ethylene polymerization in the presence of methylalumoxane (Experimental Section). Exposure of a solution of **3** and approximately 200 equiv of methylalumoxane in toluene to an atmosphere of ethylene gas resulted in the evolution of heat and the production of low-molecular-weight polyethylene (M_n = 3293, M_w/M_n = 3.1 *vs* a polyethylene standard).

Summary

In summary, the successful synthesis of a [1]boratazirconocene complex may be ascribed to the singular reactivity of ZrCl$_4$(SMe$_2$)$_2$ toward ((trimethylsilyl)cyclopentadienyl)boranes. We believe that presence of the Lewis base SMe$_2$ is crucial to promoting *ansa*-metallocene formation, as opposed to formation of a boron-bridged bimetallic complex, since, by binding to the boron bridge, the Lewis base reduces the amount of strain involved in chelation of the ligand about a single metal center. Besides the functions normally served by the interannular bridge of *ansa*-metallocene complexes, such as enforcing a rigid geometry about the metallocene by restricting rotation of the cyclopentadienyl rings[34] and altering the reactivity of the metallocene by widening the area of the “equatorial wedge”,[35,36] a boron bridge has the potential to serve other useful functions. For example, it can serve as an internal Lewis-acidic site that can participate in the chemistry of the transition metal, and it can provide a flexible joint with which to vary the overall metallocene geometry through the reversible binding of a Lewis base to the boron. The useful application of these functions will depend on our ability to replace the chlorine atoms on the zirconium with more reactive ligands. The successful alkylation of **3** by alkyllithium and alkylmagnesium reagents and the activation of **3** toward ethylene polymerization by methylalumoxane are promising results in this regard.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques. All solvents were distilled under nitrogen over sodium benzophenone ketyl (toluene, methylcyclohexane) or CaH$_2$ (methylene chloride, petroleum ether). The solvents were then stored in line-pots from which they were either vacuum-transferred from sodium benzophenone ketyl or cannulated directly. Benzene-d_6 and CDCl$_3$ were dried over activated 4 Å molecular sieves for use as NMR solvents. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. Dimethylsulfide (Aldrich) was used as received. Compound **1**,[30] ZrCl$_4$(SMe$_2$),[31] and PMe$_3$[45,46] were prepared as described in the literature.

NMR spectra were recorded on an IBM NR-300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 78 MHz, ^{31}P; 96 MHz, ^{11}B) an IBM NR-200 (200 MHz, ^{1}H; 50 MHz, ^{13}C; 64 MHz, ^{11}B), and a Varian Gemini 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C). All chemical shifts are reported in ppm and referenced to solvent (^{13}C, ^{1}H), B(OH)$_3$ (^{11}B, external reference, δ 0 ppm), or H$_3$PO$_4$ (^{31}P, external reference, δ 0 ppm). Mass spectra were obtained on a VG 7070-

---

[44] Stelck, D. S.; Basickes, N; Shapiro, P. J. Manuscript in preparation.

[45] Sharp, P. R. *Organometallics* **1984**, *3*, 1217.

[46] Wolfsberger, W.; Schmidbauer, H. *Synth. React. Inorg. Met-Org. Chem.* **1974**, *4*, 149.

HS GC/MS instrument with a heated direct-insertion probe for solid samples. FT Raman spectra were obtained on a Perkin-Elmer 2000 near-IR FT-Raman instrument. Elemental analyses were determined by Desert Analytics (Tucson, AZ).

Procedures. $\{Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2\cdot toluene$ (2). $ZrCl_4(SMe_2)_2$ (2.0 g, 5.6 mmol) was added to a solution of phenylbis((trimethylsilyl)cyclopentadienyl)boron (**1**; 2.0 g, 5.6 mmol) in 50 mL of toluene, and the reaction mixture was heated at 70 °C overnight. While the reaction mixture was still warm, it was filtered to remove any insolubles. The clear, yellow-green solution was then cooled at −78 °C to afford green crystals of **2** (yield 0.93 g, 33%). ^1H NMR (200 MHz, 297 K, $CDCl_3$): δ 7.65−7.70 (m, 2H, C_6H_5B), 7.39−7.44 (m, 3H, C_6H_5B), 7.13−7.28 (m, $C_6H_5CH_3$), 6.84 (br, 1H, $(C_5H_4)_2B$), 6.75 (br, 1H, $(C_5H_4)_2B$), 5.89 (br, 1H, $(C_5H_4)_2B$), 5.62 (br, 1H, $(C_5H_4)_2B$), 2.31 (s, $C_6H_5CH_3$), 2.11 (s, $(CH_3)_2S$). $^{13}C\{^1H\}$ NMR: δ 135.8, 128.4, 127.9 ($C_6H_5CH_3$), 129.0, 128.2, 127.2 (C_6H_5B), 125.3, 125.0, 114.9, 111.2 ($(C_5H_5)_2B$), 21.4 ($C_6H_5CH_3$), 18.29 ($(CH_3)_2S$). ^{11}B NMR (*vs* external $B(OH)_3$): δ −20. Anal. Calcd for $C_{24}H_{27}BCl_2SZr$: C, 56.38; H, 5.22. Found: C, 56.13; H, 5.03.

Attempt To Alkylate $ZrCl_4$ prior to Attaching Ligand 1. In a manner similar to that described by Thiel and Krüger for the synthesis of $ZrCl_2Me_2(bpy)$,[47] 4.7 mL of a 2 M solution of dimethylzinc in toluene was added to a stirred solution of $ZrCl_4$ (2.18 g, 9.35 mmol) in 30 mL of dimethyl sulfide at −78 °C. The reaction mixture was warmed to 0 °C, stirred for 1 h, and filtered to remove the $ZnCl_2$ precipitate. The dimethyl sulfide was removed from the filtrate *in vacuo*, and the resulting yellow residue was dissolved in 40 mL of toluene. The solution was cooled to −78 °C, and ligand **1** (3.41 g, 9.35 mmol) was added. The reaction mixture was warmed to 0 °C and stirred at that temperature for 4 h. Addition of 40 mL of petroleum ether to the reaction solution precipitated a white powder which was isolated by filtration (yield 1.06 g). On the basis of ^1H and ^{13}C NMR data, C/H analysis, and mass spectral analysis, the white powder was identified as $(C_5H_4SiMe_3)ZrCl_3\cdot SMe_2$. ^1H NMR (200 MHz, C_6D_6): δ 6.64 (m, 2H, $C_5H_4SiMe_3$), 6.57 (m, 2H, $C_5H_4SiMe_3$), 2.21 (s, 6H, $(CH_3)_2S$), 0.40 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR: δ 132.4, 126.4, 123.5 ($C_5H_4SiMe_3$), 21.2 ($CH_3)_2S$), −0.26 ($(CH_3)_3Si$). MS (EI): *m/z* 319 ($M^+ - Me - SMe_2$, 100), 303 ($M^+ - 2Me - SMe_2$, 27.7), 73 ($SiMe_3^+$, 20.0), 62 (Me_2S^+, 11.0), 53 (14.4). Anal. Calcd for $C_{10}H_{19}BCl_3SSiZr$: C, 30.25; H, 4.82. Found: C, 29.46; H, 4.50.

$\{Ph(Me_3P)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2$ (3). Trimethylphosphine (0.71 mL, 13 mmol) was condensed into a solution of **2** (3.00 g, 5.64 mmol) in 40 mL of methylene chloride at −78 °C. When the reaction mixture was warmed to room temperature, the sparingly soluble **3** dissolved completely to form a bright yellow solution. The solution was concentrated to half its original volume, and 30 mL of petroleum ether was condensed onto it at −78 °C, yielding a canary yellow solid which was collected by filtration and washed several times with petroleum ether (yield 2.41 g, 94%). ^1H NMR (200 MHz, 297 K, $CDCl_3$): δ 7.62−7.72 (m, 2H, C_6H_5B), 7.28−7.39 (m, 3H, C_6H_5B), 6.82 (m, 2H, $(C_5H_4)_2B$), 6.73 (m, 2H, $(C_5H_4)_2B$), 5.70 (m, 4H, $(C_5H_4)_2B$), 1.44 (d, 9H, $^2J_{PH} = 10.5$ Hz, $(CH_3)_3P$). $^{13}C\{^1H\}$ NMR: δ 135.5, 127.8, 126.8, 124.6 (C_6H_5B), 115.8, 115.9, 111.8 ($(C_5H_4)_2B$), 9.9 (d, $^1J_{CP} = 37$ Hz, $(CH_3)_3P$). ^{11}B NMR (*vs* external $B(OH)_3$): δ −28. ^{31}P (*vs* external H_3PO_4): δ −14.8, d, $^1J_{BP} = 64$ Hz.

Ethylene Polymerization Studies. With Compound 2. Toluene (15 mL) was added to a 227:1 mixture of methylalumoxane (0.792 g) and **2** (0.030 g) in a 50 mL thick-walled glass vessel. An atmosphere of ethylene was admitted to the vacuum manifold (corresponding to a volume of approximately 1 L) and condensed into a liquid-nitrogen-cooled trap. The ethylene was thawed, refrozen, and subjected to a dynamic vacuum twice in order to remove any trapped oxygen. It was then rethawed and condensed into the reaction vessel, which was cooled in liquid nitrogen. The reaction vessel was warmed to room temperature. There was no appearance of polymer or any evolution of heat from the reaction mixture. No change was noticed after the reaction mixture was stirred overnight at room temperature, and no ethylene consumption appeared to have occurred when the ethylene was released from the reaction vessel to the vacuum manifold.

With Compound 3. Toluene (50 mL) was added to a 249:1 mixture of methylalumoxane (0.70 g) and **3** (0.025 g) in a 100 mL Schlenk flask. Ethylene gas was passed through the flask at atmospheric pressure while the reaction mixture was stirred at room temperature. Heat evolved from the reaction mixture as it turned from clear yellow to cloudy. The flask was purged with ethylene in this manner for approximately 5 min, and then the reaction was quenched with 5 mL of methanol. The removal of all volatiles under vacuum left a powdery, white solid which was washed repeatedly with water, followed by 6 M HCl in order to remove any acid-soluble material, followed by water and concentrated aqueous NaOH in order to remove any base-soluble material. After a final wash with water and acetone, the solid was air-dried to give 2.5 g of a fine white powder. This powder exhibited an FT Raman spectrum identical with that of a high-density polyethylene standard. GPC analysis of the polymer (*vs* a polyethylene standard) gave $M_w = 10\,200$ and $M_n = 3293$, for a PDI value of 3.1.

X-ray Crystal Structure Determinations of 2 and 3. Crystals of compounds **2** and **3**, grown from NMR tube samples in C_6D_6 and $CDCl_3$, respectively, were mounted in thin-walled glass capillaries under an N_2 atomosphere. Crystals of both compounds were determined from diffraction symmetry to belong to the orthorhombic crystal system. Data were collected using a Siemens P4 diffractometer equipped with a SMART CCD area detector. Systematic absences in the diffraction data were uniquely consistent for *Pbca* for **3** and either $Pna2_1$ or *Pnam* (nonstandard setting of *Pnma*) for **2**. For **2**, the centrosymmetric space group was chosen based on *Z*, the distribution of *E* factors, and the clear presence of a molecular mirror plane aligned with the crystal axes. This choice was substantiated by the results of refinement. An empirical correction for absorption was made for each structure. The structures were solved by direct methods and completed from difference Fourier maps. A molecule of benzene, the recrystallization solvent, was located in the crystal lattice for **2**. All computations used SHELXTL 5.1 software (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We thank Prof. Wayne Tikkanen (CalState LA) for key experimental advice, Mr. Bryan Bowie (University of Idaho) for FT Raman characterization of the polyethylene (Supporting Information), Dr. Gregory T. Whiteker (Union Carbide) for a GPC analysis of the polyethylene, Prof. John Bercaw (Caltech) for a donation of toluene-free methylalumoxane (Albemarle), and Dr. Gary Knerr (University of Idaho) for assistance with obtaining NMR spectra. This research was supported by the National Science Foundation (Grant No. CHE-9320407) and the NSF Idaho EPSCoR program (Grant No. EPS 9350539).

Supporting Information Available: Tables of crystallographic data collection and solution and refinement details, atomic coordinates, all bond lengths and angles, and anisotropic displacement coefficients for compounds **2** and **3** and an FT Raman spectrum and a GPC analysis of polyethylene produced with **3** (15 pages). Ordering information is given on any current masthead page.

OM970253+

---

[47] Thiele, V. K.-H.; Krüger, J. *Z. Anorg. Allg. Chem.* **1971**, *383*, 272−278.