5432 *Organometallics* **1999,** *18,* 5432−5434

Stable Borate-Bridged *ansa*-Zirconocene Complexes. Preparation and X-ray Crystallographic Characterization of [Cp*$_2$Al]$^+$[Me(Ph)B(η^5-C$_5$H$_4$)$_2$ZrCl$_2$]$^-$ and [PPN]$^+$[Cl(Ph)B(η^5-C$_5$H$_4$)$_2$ZrCl$_2$]$^-$

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Received September 21, 1999

*Summary: The title complexes are stable, borate-bridged ansa-zirconocene species which have been prepared by reacting [{Ph(SMe$_2$)B(η^5-C$_5$H$_4$)$_2$}ZrCl$_2$] (**1**) with Cp*$_2$-AlMe and [PPN]Cl. Their molecular structures were determined by X-ray diffraction. Noteworthy are the stabilities of the borate−cyclopentadienyl linkages and the enhanced Lewis acidity of the boron within its strained ansa position.*

The covalent attachment of boryl groups to the cyclopentadienyl or indenyl rings of group 4 metallocene and half-sandwich complexes is a strategy that has been pursued by ourselves and by others[1] with a variety of goals in mind, the most popular one being the development of well-defined, single-component, zwitterionic olefin polymerization catalysts as alternatives to the traditional, two-component systems. Incorporation of the boryl group in the interannular bridging position between the cyclopentadienyl rings has been of particular interest to us, because it offers the additional prospect of using reversible Lewis base coordination by the boron bridge to manipulate the geometry of the metallocene as well as to anchor special functionalities to the metallocene.

One of the drawbacks that we[1d,i] and others[1k] have faced in developing the chemistry of boryl-substituted metallocenes is the vulnerability of the boryl group to cleavage from the cyclopentadienyl ring. This typically occurs in the presence of anionic nucleophiles such as metal alkyls, which are an essential feature in the transition-metal chemistry of interest to us. Such problems with cleavage of the boryl group from the ligand framework beset our earlier efforts to alkylate various half-sandwich boryl−cyclopentadienyl titanium and zirconium complexes and are probably responsible for the decomposition we have encountered upon trying to alkylate our boron-bridged *ansa*-zirconocene complexes. Indeed, whereas treatment of [Ph(SMe$_2$)B(η^5-C$_5$H$_4$)$_2$ZrCl$_2$] with alkyllithium, alkyl Grignard, dialkylzinc, or trialkylaluminum reagents leads to decomposition, presumably due to the lability of the dimethyl sulfide adduct, substitution of the dimethyl sulfide ligand with a more tightly coordinating trimethylphosphine enables alkylation of the zirconium center by these reagents to cleanly form complexes of the type [{Ph(PMe$_3$)B(η^5-C$_5$H$_4$)$_2$}ZrR$_2$] (R = CH$_2$SiMe$_3$, CH$_2$C$_6$H$_5$).[1i] Unfortunately, blocking or attenuating the electrophilicity of the boron bridge is a less than ideal solution for us, since it defeats some of the anticipated applications we have for these complexes. We now report the isolation of stable, borate-bridged *ansa*-zirconocene complexes which appear to belie the assumed instability of the borate group to cleavage from the cyclopentadienyl ring and offer renewed hope for our developing further the chemistry of these complexes.

Reaction of the *ansa*-zirconocene complex [{Ph(PMe$_3$)B(η^5-C$_5$H$_4$)$_2$}ZrCl$_2$] (**1**) with Cp*$_2$AlMe (Cp* = C$_5$Me$_5$), a new compound recently developed in our laboratories,[2] produced the ionic complex [Cp*$_2$Al]$^+$[{Ph(Me)B(η^5-C$_5$H$_4$)$_2$}ZrCl$_2$]$^-$ (**2**),[3] in which a methyl anion from the aluminum had been completely transferred to the boron

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[1] (a) Reetz, M. T.; Brümmer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501. (b) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (c) Rufanov, K. A.; Kotov, V. V.; Kazennova, N. B.; Lemenovskii, D. A.; Avtomonov, E. V.; Lorberth, J. *J. Organomet. Chem.* **1996**, *525*, 287. (d) Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2393. (e) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (f) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. (g) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995. (h) Rufanov, K.; Avtomonov, E.; Kazennova, N.; Kotov, V.; Khvorost, A.; Lemenovskii, D.; Lorberth, J. *J. Organomet. Chem.* **1997**, *536−537*, 361. (i) Stelck, D. S.; Shapiro, P. J.; Basickes, N. *Organometallics* **1997**, *16*, 4546. (j) Rufanov, K.; Avtomonov, E.; Kazennova, N.; Kotov, V.; Khvorost, A.; Lemenovskii, D.; Lorberth, J. *J. Organomet. Chem.* **1997**, 536−537, 361. (k) Shafiq, F. A.; Abboud, K. A.; Richardson, D. E.; Boncella, J. M. *Organometallics* **1998**, *17*, 982. (l) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829. (m) Braunschweig, H.; von Koblinski, C.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 69. (n) Ashe, A. J.; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288. (o) Reetz, M. T.; Willuhn, M.; Psiorz, C.; Goddard, R. *Chem. Commun.* **1999**, 1105. (p) Starzewski, K. A. O.; Kelly, W. M.; Stumpf, A.; Freitag, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2439.

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10.1021/om990744p CCC: $18.00

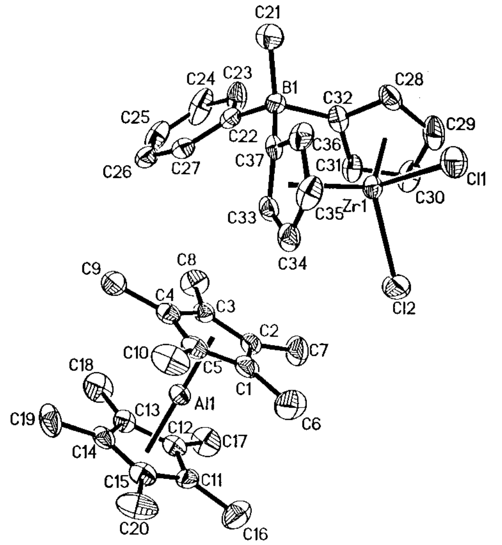
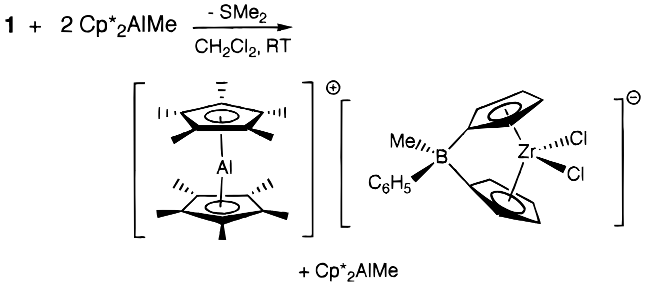


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): B−C21 = 1.626(8), B−C32 = 1.639(8); cent−Zr−cent = 120.5, cent−Al−cent = 178.6, C32−B−C37 = 97.2(4).

bridge (eq 1). Probably due to a competitive equilibrium



with the dimethyl sulfide released in the reaction, approximately 2 equiv of $Cp*_2AlMe$ is required to drive the reaction to completion. The remaining, unreacted $Cp*_2AlMe$ is then washed away from **2** with petroleum ether. The molecular structure of the ion pair was determined by single-crystal X-ray diffraction methods and is shown in Figure 1.[4]

The structure of the rather exotic aluminocenium countercation is similar to that determined previously by Schnöckel and co-workers for $[Cp*_2Al][Cp*AlCl_3]$.[6] The absence of any residual interactions between the aluminocenium cation and the methyl anion in the solid state is evidenced by the fact that the nearest Al- - -C(21) contact is nearly 6 Å. The possibility of any interaction between the aluminocenium cation and a chlorine ligand on zirconium can also be ruled out since the closest Al- - -Cl contact is 5.8 Å. Within the *ansa*-zirconocene counteranion, the Cp−B−Cp angle of the borate bridge of 97.2° is considerably narrower than the corresponding angle in **1** (101.1°) and the trimethylphosphine adduct $[Ph(PMe_3)B(\eta^5\text{-}C_5H_4)_2ZrCl_2]$ (100.1°).[1i] The (ring centroid)−Zr−(ring centroid) angle of 120.5° for **2** is only slightly narrower than that of the other complexes (121.1 and 121.3°, respectively). The bond distance between the boron and methyl carbon of 1.626(8) Å is even shorter than the corresponding distance of 1.638(5) Å found for a "free" $[MeB(C_6F_5)_3]^-$ counteranion and is considerably shorter than that of associated borate counteranions in a series of cationic zirconocene complexes reported by Marks and co-workers.[5] That complete methyl anion transfer is maintained in solution is supported by the ^{27}Al NMR spectrum of the complex, which exhibits a sharp peak at δ −114.5 characteristic of the permethylaluminocenium cation.[6] The ^1H NMR spectrum of **2** in $CDCl_3$ exhibits a signal at δ 0.31 for the borate methyl group, as compared to δ −1.58 for the Al−methyl resonance of $Cp*_2AlMe$. There is a broad signal at δ 10 in the ^{13}C NMR spectrum of **2** which is partially obscured by the methyl resonance of the aluminocenium cation. We tentatively assign this to the methyl carbon of the borate bridge.

The stability of the methylphenylborate bridge in **2** was surprising to us for the reasons mentioned above. The only decomposition we observe in a room-temperature $CDCl_3$ solution sample of **2** over time involves the gradual decomposition of the aluminocenium cation via the elimination of Cp*H, a decomposition which we observe with other decamethylaluminocenium salts.[2] In contrast, a similar reaction between **1** and Cp_2AlMe in $CDCl_3$ monitored by ^1H NMR spectroscopy revealed complete conversion of the reactants to an ill-defined mixture of products. Unlike **1**, complex **2** is activated by an excess of methylalumoxane toward the polymerization of ethylene with an activity of 902 kg of PE/((mol of catalyst) bar h) (cf. $[\{(Ph)(PMe_3)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$, which has an activity of 1664 kg of PE/((mol of catalyst) bar h)).[7]

We attribute the stability of **2** to the bulky, nonintrusive nature of the decamethylaluminocenium countercation. This countercation effect could perhaps also explain why $[Li(THF)_4][C_5H_5B(C_6F_5)_3]$ and $[NEt_4][C_5H_5B(C_6F_5)_3]$ are successfully zirconated to form the corresponding borato−cyclopentadienyl zirconium complexes,[11] whereas attempted zirconation of $Li[1,3\text{-}Me_3SiC_5H_4B(C_6F_5)_3]$ led instead to the elimination of $Li[MeB(C_6F_5)_3]$.[1k] Guided by this hypothesis, we have since prepared a variety of other stable borate-bridged *ansa*-zirconcene species by reacting **1** with salts of other bulky cations such as tetrabutylammonium and bis(triphenylphosphoranylidene)ammonium ($[PPN]^+ = [(Ph_2P)_2N]^+$). One of these salts, $[PPN]^+[\{Ph(Cl)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]^-$

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(3) ^1H NMR (500.13 MHz, $CDCl_3$): δ 7.77 (d, 2H, $o\text{-}C_6H_5B$, $^3J_{HH}$ = 7 Hz), 7.23 (pseudo-triplet, 2H, $m\text{-}C_6H_5B$), 7.06 (pseudotriplet, 1H, $p\text{-}C_5H_5B$), 6.62−6.64 (two overlapping m, 4H, $(C_5H_4)_2B$), 5.84 (m, 2H, $(C_5H_4)B$), 5.65 (m, 2H, $(C_5H_4)B$), 2.19 (s, 30 H, $[C_5(CH_3)_5]_2Al$, 0.31 (s, 3H, CH_3B). $^{13}C\{^1H\}$ NMR: δ 136.4 (br, C_6H_5B-ipso), 134.5, 127.0, 126.2 (C_6H_5B), 124.2, 123.3, 115.0, 114.8 ($(C_5H_4)_2B$), 118.8 ($C_5(CH_3)_5$), 10.7 ($C_5(CH_3)_5$, 10 (br, $B(CH_3)$). ^{27}Al NMR (vs external $Al(OH)_3$): δ −114.5. ^{11}B NMR (vs external $B(OH)_3$): δ −31.6. Anal. Calcd for $C_{37}H_{46}AlBCl_2Zr$: C, 64.34; H, 6.71. Found: C, 62.39; H, 6.54. The carbon analysis was consistently low. We attribute this to $Cp*_2Al^+$ decomposition, which we were unable to completely eliminate.

(4) Crystal data: $C_{37}H_{46}AlBCl_2Zr$; space group $P2_1/n$; monoclinic; a = 13.961(2) Å, b = 17.058(3) Å, c = 14.639(2) Å, β = 93.158(10)° at 213 K; V = 3481.0(9) Å^3; Z = 4; final R indices ($I > 2\sigma(I)$) R1 = 0.0669, wR2 = 0.1265 for 7852 independent reflections.

(5) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(6) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655.

(7) The ethylene polymerizations were performed as described in: Duda, L.; Erker, G.; Fröhlich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1153.

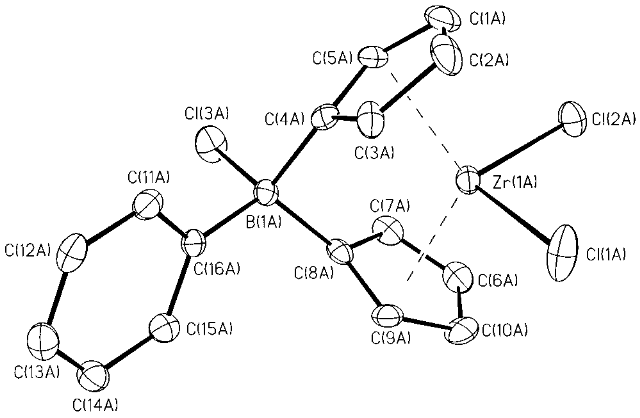

Figure 2. Molecular structure of the *ansa*-zirconocene anion of one of two independent molecules of **3** in the unit cell. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): B(1A)−Cl(3A) = 1.937(5), B(1A)−C(8A) = 1.634(7); average cent−Zr−cent = 120.9, C(4A)−B(1A)−C(8A) = 99.4(4).

(**3**),[8] has also been crystallographically characterized, and an ORTEP drawing of one of two unique *ansa*-zirconocene anions in the unit cell is shown in Figure 2.[9] The Cp−B−Cp angle is 99.4(4)°, between that of compounds **1** and **2**. An average (ring centroid)−Zr−(ring centroid) angle of 120.5° for the two unique molecules is comparable to that of **2**. This compound is stable indefinitely under an N_2 atmosphere in the solid state and in $CDCl_3$ solution. It is also activated by methylalumoxane toward ethylene polymerization, exhibiting an activity of 574 kg of PE/((mol of catalyst) bar h).

Another relevant aspect of the formation of **2** is the ability of the boron bridge of the *ansa*-zirconocene complex to abstract a methanide ion from $Cp^*{}_2AlMe$. On the basis of the C≡N IR stretching frequences for the *tert*-butyl isocyanide adducts $[\{Ph(t\text{-}BuNC)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (2272 cm^{-1}), $Ph_3B(CN\text{-}t\text{-}Bu)$ (2272 cm^{-1}), and $(C_6F_5)_3B(CN\text{-}t\text{-}Bu)$ (2310 cm^{-1}),[10] one would expect the reactivity of the phenylboron bridge to be similar to that of BPh_3. However, BPh_3 is unreactive toward $Cp^*{}_2AlMe$, as determined from the absence of either ^1H or ^{27}Al NMR spectral evidence for the formation of $[Cp^*{}_2Al]^+$ when $Cp^*{}_2AlMe$ is combined with triphenylborane in $CDCl_3$. In constrast, the phenylboron bridge is comparable to $B(C_6F_5)_3$ in its reactivity. To assess the effective Lewis acidity of the boron bridge in base free $[PhB(C_5H_4)_2ZrCl_2]$, **1** was combined with an equimolar amount of $B(C_6F_5)_3$ in CD_2Cl_2 and the ratio of base-free $B(C_6F_5)_3$ to $(C_6F_5)_3B(SMe_2)$ was determined by ^{19}F NMR. Interestingly, the ratio of base-free to coordinated $B(C_6F_5)_3$ was found to be 1.7:1 at 273 K, indicating that the boron bridge of the *ansa*-zirconocene has a higher affinity for the dimethyl sulfide ligand than $B(C_6F_5)_3$. Similarly, combination of $[\{Ph(tBuNC)B(C_5H_4)_2\}ZrCl_2]$ with a equimolar amount of $B(C_6F_5)_3$ produced a 2.1:1 ratio of base-free to coordinated $B(C_6F_5)_3$ at 263 K.[11] The combined results suggest that the "internal strain" experienced by the sp^2-hybridized boron atom incorporated into the bridging position of an *ansa*-zirconocene complex raises the Lewis acidity of the boron bridge to a level comparable to that of $B(C_6F_5)_3$.

In summary, the important lessons that we have learned from the isolation of the title complexes are (a) that a borate-derivatized cyclopentadienyl ring on a transition metal can be stable in the presence of a suitably bulky, noninteracting countercation and (b) that the Lewis acidity of a boron species can be enhanced substantially by introducing strain in the molecule which can be relieved through the coordination of Lewis bases which rehybridize the boron from sp^2 to sp^3. We are using these lessons to develop additional examples of borate-bridged *ansa*-zirconocene complexes and to aid us in our pursuit of useful catalysis with these complexes.

Acknowledgment. Support of this work by the NSF Idaho EPSCoR program (Grant No. EPS 9350539) and a University of Idaho Seed grant are gratefully acknowledged. P.J.S. is also grateful to the Alexander von Humboldt Foundation for a fellowship supporting a six-month sabbatical in the research group of Prof. Dr. Gerhard Erker, during which some of the results reported in this paper were obtained.

Supporting Information Available: Text giving experimental descriptions for the synthesis of $Cp^*{}_2AlMe$, **2**, and **3**, a figure giving the ^{19}F NMR spectrum of a 1:1 mixture of **1** and $B(C_6F_5)_3$ in CD_2Cl_2, and tables of crystal data, thermal parameters, bond distances, bond angles, and atomic coordinates for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] ^1H NMR (200 MHz, $CDCl_3$): δ 7.82−7.86 (m, 2H, C_6H_5B), 7.55−7.63 (m, 3H, C_6H_5B), 7.21−7.45 (m, 30H, $N[P(C_6H_5)_3]_2$), 6.57−6.64 (m, 4H, $(C_5H_4)_2B$), 6.10−6.14 (m, 2H, $(C_5H_4)_2B$), 5.44−5.48 (m, 2H, $(C_5H_4)_2B$). $^{13}C\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ 134.2, 132.3, 129.9 ($(C_6H_5)_3P$), 127.9, 127.4, 126.5 (C_6H_5B), 125.5, 125.0, 115.7, 113.2 ($(C_5H_4)_2B$). ^{11}B NMR (vs external H_3BO_3): δ −22.1. ^{31}P NMR (vs external H_3PO_4): δ 21.2. Anal. Calcd for $C_{52}H_{43}BCl_3NP_2Zr$: C, 65.59; H, 4.43; N, 1.33. Found: C, 65.41; H, 4.43; N, 1.33.

[9] Crystal data: $C_{52}H_{45}BCl_3NP_2Zr$; space group $P\bar{1}$; monoclinic; a = 13.6573(3) Å, b = 15.6301(3) Å, c = 23.2356(4) Å, α = 102.4478(6)°, β = 94.3487(7)°, γ = 105.3451(6)° at 173 K; V = 4561.74(22) $Å^3$; Z = 4 with two independent, chemically equivalent molecules in the unit cell; final R indices ($I > 2\sigma(I)$) R1 = 0.0645, wR2 = 0.1734 for 19 571 independent reflections.

[10] Jacobson, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724. This reference also reports a ν(C≡N) band for free *tert*-butyl isocyanide of 2140 cm^{-1}.

[11] We cannot say with certainty that these ratios represent true equilibrium values, since we are, as yet, unable to approach the equilibrium from the opposite direction by combining either $(C_6F_5)_3B(SMe_2)$ or $(C_6F_5)_3B(CN\text{-}t\text{-}Bu)$ with base-free $[\{PhB(C_5H_4)_2\}ZrCl_2]$. This is because we have not yet successfully isolated the base-free *ansa*-zirconocene species.[1h,i] The ^1H spectra are consistent with our interpretation of the ^{19}F spectra, and we see the appearance of a new set of AB pseudo-triplets at δ 7.13 and 6.6 in the ^1H NMR spectra, which we attribute to the cyclopentadienyl protons of the base-free *ansa*-zirconocene. There is also some evidence of decomposition of the *ansa*-zirconocene to form a B−Cp cleavage product, which we believe arises due to the instability of the base-free *ansa*-zirconocene complex. Thanks to a reviewer's suggestion, we have verified that $(C_6F_5)_3B(SMe_2)$ and $(C_6F_5)_3B(CN\text{-}t\text{-}Bu)$ do not dissociate to any detectable amounts (<1%) of free $(C_6F_5)_3B$ and ligand under similar experimental conditions. Hence, the ratios of free and coordinated $(C_6F_5)_3B$ that we observe in our competition experiments do not simply reflect the dissociation equilibria of the $(C_6F_5)_3B$ adducts.