

New Fluorinated 9-Borafluorene Lewis Acids

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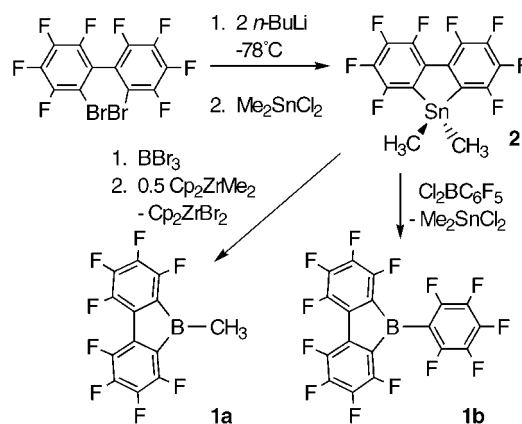
Tris(pentafluorophenyl)borane¹ and its derivatives are important Lewis acids for olefin polymerization and organic synthesis.² For both applications, Lewis acid strength is a key factor in the borane's performance. Attempts to improve the Lewis acidity of the parent B(C₆F₅)₃ borane have focused on the use of more heavily fluorinated aryl groups, e.g. perfluorobiphenyl³ or perfluoronaphthyl.⁴ While this has been shown to be effective both experimentally and computationally,⁵ the limitation of this approach lies in the increasing front- and back-strain engendered by sterically larger groups, which eventually counters the gains made by the increased electron-withdrawing power of more fluorine substituents.

A second strategy for ramping up the Lewis acid strength of a boron center is to incorporate it into a five-membered borole ring,⁶ which by virtue of the 4π electron count is antiaromatic. The tendency to remove the boron p-orbital from conjugation in the borole ring increases the boron Lewis acidity relative to noncyclic analogues;^{6,7} furthermore, the relief of strain energy in the borole ring upon boron pyramidalization also contributes to the enhanced Lewis acidity of boroles. Here we report the synthesis of the fluorinated biphenyl-based borole derivatives (C₁₂F₈)B-R [R = CH₃ (**1a**), C₆F₅ (**1b**), Br (**1c**)]⁸ and demonstrate their enhanced Lewis acidity relative to the more heavily fluorinated (C₆F₅)₂B-R analogues.

The synthetic route to 9-borafluorenes **1** is a boron–tin exchange reaction analogous to that used to prepare pentaphenylborole⁶ (Scheme 1). We have improved the published synthesis of the stannole **2**⁹ by using more dilute conditions. Reaction of this material with BBr₃ gives **1c**, which is methylated using Cp₂Zr(CH₃)₂ to give **1a** (¹¹B NMR = 67.3 ppm). Direct reaction of **2** with Cl₂BC₆F₅¹⁰ leads to the fully fluorinated 9-borafluorene **1b** (¹¹B NMR = 57.0 ppm).¹¹

Both **1a** and **1b** were characterized by NMR and UV–vis spectroscopy and the solid-state structure of **1b** was determined

Scheme 1



via X-ray crystallography (Figure 1).¹² The boron center is planar ($\Sigma_{C-B-C} = 360.0^\circ$) but the C(5)–B(1)–C(5*) angle is compressed to 103.6(2)°. The borafluorene ring is essentially planar, and the C₆F₅ ring is tilted out of this plane by 53.2(1)°, precluding conjugation between the aryl and 9-borafluorene π systems. In contrast to the blue pentaphenylborole ($\lambda_{\max} = 570$ nm, $\pi \rightarrow \pi^*$),⁶ compounds **1** are pale yellow or orange in color (λ_{\max} **1a**, 398 nm; **1b**, 440 nm), comparable to the nonfluorinated 9-borafluorene analogues⁸ ($\lambda_{\max} = 385$ –405 nm).

Several observations show that 9-borafluorenes **1a** and **1b** are slightly stronger Lewis acids than their bis-pentafluorophenyl analogues (i.e. H₃CB(C₆F₅)₂¹³ and B(C₆F₅)₃). In a competition reaction, **1b** competes more effectively for acetonitrile compared to B(C₆F₅)₃.¹⁴ Marks et al. has used the Childs method¹⁵ to situate a variety of perfluoroaryl boranes on a scale containing a variety of main group Lewis acids (relative to BBr₃ at 1.00).^{2a} By this method, **1a** has a relative value of 0.58 ± 0.02 (cf. the value of 0.56 ± 0.02 for H₃CB(C₆F₅)₂) and **1b** places at 0.70 ± 0.02 (cf. 0.68 ± 0.02 for B(C₆F₅)₃).¹⁶ Finally, Laszlo and Teston used semiempirical MNDO calculations to compute the energy of the π* molecular orbital in LA·crotonaldehyde adducts, which is related to the Childs Lewis acidity.¹⁷ Again, **1a** and **1b** prove to be stronger Lewis acids than RB(C₆F₅)₂.¹¹ Thus, the antiaromatic nature of the central borole moiety more than compensates for the loss of two fluorine atoms.⁵ Using these data and that published by Marks et al.,^{2a} a relative scale of Lewis acidity for a variety of perfluorinated boranes and 9-borafluorenes **1** (toward crotonaldehyde) is PBB > PNB > **1b** > B(C₆F₅)₃ ≫ **1a** > H₃CB(C₆F₅)₂.

There is a wealth of potential applications for these compounds, not only as Lewis acids, but also as electron deficient ligands.¹⁸ In terms of metallocene activation, both **1a** and **1b** are effective

(11) Attempts to prepare **1b** directly from the 2,2'-dilithio-perfluorobiphenyl reagent and Cl₂B(C₆F₅) led to isolation of the Et₃O adduct of **1b**; the base could not be removed under conditions which did not decompose the compound.

(12) For full details see the Supporting Information.

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(14) At room temperature $K_{\text{eq}} = 1.30(3)$ for B(C₆F₅)₃·NCCH₃ + **1b** ⇌ **1b**·NCCH₃ + B(C₆F₅)₃.

(15) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(16) Marks et al. report a value of 0.77 on the Child's scale for B(C₆F₅)₃.^{2a} While the value we obtain is somewhat lower, it is consistent with the order of Lewis acidity obtained for **1b** and B(C₆F₅)₃ based on the competition and computational experiments described.

(17) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.

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[†] University of Calgary.[‡] University of British Columbia.(1) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218.(2) (a) Chen, Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 345. (c) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527.(3) (a) Chen, Y. X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (b) Li, L.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 3332.(4) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996.(5) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.(6) (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (b) Sebald, A.; Wrackmeyer, B. *J. Organomet. Chem.* **1986**, *307*, 157. (c) Herberich, G. E.; Buller, G.; Hessner, B.; Oschmann, W. *J. Organomet. Chem.* **1980**, *195*, 249.(7) Antiaromaticity also plays a role in the high Lewis acidity observed in perfluorinated 9,10-boraanthracenes: (a) Williams, V. C.; Dai, C.; Liz, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695. (b) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312.(8) Nonfluorinated 9-borafluorenes have been reported: Köster, R.; Benedikt, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 323.(9) Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1967**, *10*, 471.(10) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, 3933.

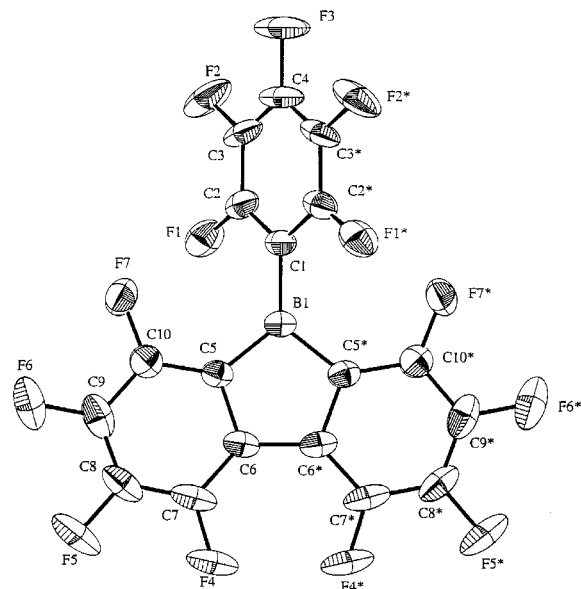
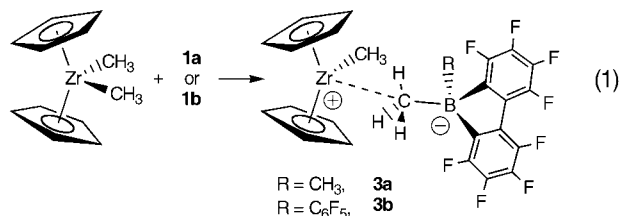


Figure 1. ORTEP diagram of **1b** (50% ellipsoids). Selected bond distances (Å): B(1)–C(1), 1.556(4); B(1)–C(5), 1.549(3); C(5)–C(6), 1.424(3); C(6)–C(6*), 1.481(4). Selected bond angles (deg): C(1)–B(1)–C(5), 128.2(1); C(5)–B(1)–C(5*), 103.6(2); B(1)–C(5)–C(6), 108.7(2); B(1)–C(5)–C(10), 131.7(2); C(5)–C(6)–C(6*), 109.5(1); C(7)–C(6)–C(6*), 131.7(1).

and reaction of both **1a** and **1b** with $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ leads to rapid ion pair formation (eq 1). The structure of contact ion pair **3a**



(an ORTEP diagram is shown in Figure 2) has similar features to those found for ion pairs involving the $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ ion.^{2a} The $[(\text{H}_3\text{C})_2\text{B}(\text{C}_6\text{F}_5)_2]^-$ anion contacts the metalocenium ion through only one of its methyl groups and the bridging methyl group is more closely associated with boron (B(1)–C(1) = 1.666(5) Å, cf. B(1)–C(2) = 1.625(4) Å) than zirconium (Zr(1)–C(1) = 2.506(3) Å, cf. Zr(1)–C(15) = 2.252(4) Å), suggesting that **1a** has effected substantial abstraction of the methide anion despite its comparatively low Lewis acidity. The boron center is now pyramidalized to a distorted tetrahedron; the C(3)–B(1)–C(14) angle is 97.2(2)°.

According to the solid state structure, three chemically distinct methyl groups should be apparent in solution; however, at 25 °C the methyl groups rapidly exchange on the NMR time scale. At –60 °C, the broad signal ascribed to the CH_3 groups resolves into three at 0.32 (Zr– CH_3), 0.74 (B– CH_3 term), and 0.02 ppm (B– CH_3 bridge). Although fluxional, **3a** is remarkably stable in toluene solution, persisting for several days. This contrasts with the behavior of the ion pair formed from $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ and $\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_2$, for which facile back transfer of a $-\text{C}_6\text{F}_5$ group is observed under similar conditions to give $(\text{H}_3\text{C})_2\text{B}(\text{C}_6\text{F}_5)$ and $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{C}_6\text{F}_5$.¹³ This observation reveals another potential advantage of these compounds: anion stability. Thus, while the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\mathbf{1a}$ and $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_2$ catalyst systems

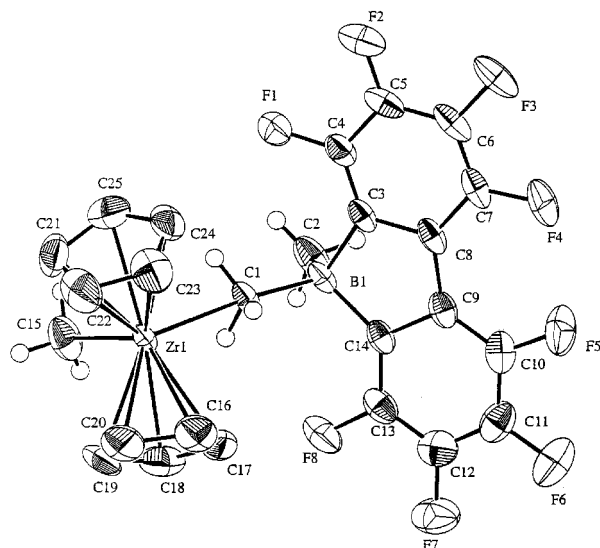


Figure 2. ORTEP diagram of **3a** (50% ellipsoids). Selected bond distances (Å): B(1)–C(1), 1.666(5); B(1)–C(2), 1.625(4); B(1)–C(3), 1.635(4); B(1)–C(14), 1.617(4); Zr(1)–C(1), 2.506(3); Zr(1)–C(15), 2.252(4). Selected bond angles (deg): C(15)–Zr(1)–C(1), 96.0(1); Zr(1)–C(1)–B(1), 169.5(2); C(1)–B(1)–C(2), 110.7(3); C(1)–B(1)–C(3), 111.5(2); C(1)–B(1)–C(14), 113.0(2); C(2)–B(1)–C(3), 111.8(2); C(2)–B(1)–C(14), 112.1(2); C(3)–B(1)–C(14), 97.2(2).

behave comparably in terms of ethylene polymerization activity at 25 °C,¹⁹ the latter is rapidly deactivated when polymerizations are conducted after a 5 min incubation period at 70 °C. Due to the chelate effect, aryl transfer is precluded and the ion pair **3a** is much more robust under these conditions,²⁰ retaining its activity ($2.3(3) \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$). 9-Borafluorene Lewis acid **1a** is the prototypical member of a new class of activators for olefin polymerization processes which contain only two fluorinated aryl groups and produce anions that do not undergo deactivation via aryl transfer.²¹ Ion pair **3b** is also highly stable in solution in the absence of monomer; this catalyst system is approximately twice as active ($4.6(3) \times 10^5 \text{ g mol}^{-1} \text{ h}^{-1}$) as the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalyst system ($2.7(3) \times 10^5 \text{ g mol}^{-1} \text{ h}^{-1}$) under identical conditions.

In conclusion, we have developed a route to a new family of fluorinated 9-borafluorene Lewis acids and demonstrated their application in metallocene activation. We are currently continuing in this vein, in addition to examining their electrochemistry, their efficacy as Lewis acids for organic synthesis, and the coordination chemistry of the borollides.

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Supporting Information Available: Experimental and spectroscopic details for new compounds and tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1b** and **3a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Activities for these two catalyst systems fall in the range [1.9–2.3(3)] $\times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$.

(20) With prolonged heating, ion pair **3a** undergoes a different decomposition process involving methane loss.

(21) This is also a common deactivation pathway for the $[\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$ and to a lesser extent the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions.^{2a} A borate anion with two C_{12}F_8 groups attached to boron is mentioned in ref 2a and also capitalizes on the chelate effect. See also: Bohnen, H.; Fritze, C.; Kuber, F. PCT International Patent Application WO 9943685, 1999.