

New Bifunctional Perfluoroaryl Boranes. Synthesis and Reactivity of the *ortho*-Phenylene-Bridged Diboranes 1,2-[B(C₆F₅)₂]₂C₆X₄ (X = H, F)[†]

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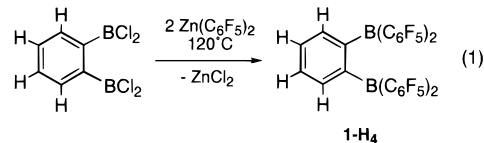
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Highly electrophilic boranes containing perfluorinated aryl groups are effective activators for olefin polymerization using d₀ transition metal catalysts.¹ To date, the most effective examples² have been monofunctional boranes, but it has been suggested that bifunctional Lewis acids might offer advantages since the counterions formed from diboranes are potentially less coordinating than [RB(Ar_F)₃]⁻.³ To this end, we have been developing routes to various diboranes of general formula (C₆F₅)₂B-linker-B(C₆F₅)₂ for testing as metallocene activators. Although such compounds are most relevant in the olefin polymerization arena, in a more general sense bifunctional boron-based Lewis acids are finding application in such diverse areas as organic synthesis,⁴ new materials,⁵ selective anion binding,⁶ and molecular recognition.⁷ Thus far, diboranes incorporating B(C₆F₅)₂ units have been limited to those with one-carbon linkers,^{3a,8} which have some limitations and are, at any rate, best suited to binding hydride anions. Herein we report synthetic routes to diboranes containing bis-(pentafluorophenyl)boryl groups tethered by the two-carbon periprotio and perfluoro *ortho*-phenylene bridges.

Recently, we reported the molecular structure of the base-free zinc compound Zn(C₆F₅)₂,⁹ which we tested as a -C₆F₅ transfer agent.¹⁰ While it was not selective in reactions with BCl₃, it is an effective reagent for converting -BCl₂ units to -B(C₆F₅)₂ groups.

Thus, treatment of the known compound 1,2-(BCl₂)₂C₆H₄¹¹ with slightly more than 2 equiv of Zn(C₆F₅)₂ led to smooth conversion to the desired product **1-H₄**¹² as shown in eq 1. While the first



two -C₆F₅ groups are incorporated relatively easily, the third and fourth substitutions require heating to 120 °C to ensure complete C₆F₅ transfer. ¹H NMR spectra of the reaction in progress revealed the sequential nature of the substitution process eventually yielding **1-H₄**, characterized by a complex multiplet centered around 7.73 ppm for the aromatic protons of the symmetrical AA'BB' phenylene backbone. In addition to full spectroscopic characterization, the molecular structure of **1-H₄** has been determined (see Supporting Information).

Boranes of general formula RB(C₆F₅)₂ are prone to proteolytic loss of RH¹³ and are less Lewis acid than B(C₆F₅)₃;¹⁴ furthermore, anions formed via methyl abstraction using such boranes (i.e., [R(CH₃)B(C₆F₅)₂]⁻) are unstable toward transfer of C₆F₅ groups back to the metal.⁸ Indeed, **1-H₄** suffers from some of these problems in addition to being poorly soluble in aromatic solvents, which are usually employed in solution olefin polymerization processes. Accordingly, a more desirable *ortho*-phenylene-bridged diborane would include a fully fluorinated backbone which, like the parent borane B(C₆F₅)₃, should be more stable to proteolysis¹⁵ and -C₆F₅ transfer and offer better solubility properties. The fully fluorinated analogue of **1**, i.e., **1-F₄**, however, represents a more formidable synthetic challenge since the deactivating effect of four fluorine substituents precludes the use of a route analogous to that employed for preparing **1-H₄**. Not only were we unable to prepare 1,2-(Me₃Si)₂C₆F₄ but a model reaction between BCl₃ and C₆F₅SiMe₃ showed also that the silyl methyl groups preferentially underwent metathesis to boron instead of the required C₆F₅.

We thus turned to the known mercury trimer [(C₆F₄)Hg]₃¹⁶ as a synthon for installing the 1,2-BX₂ units on the tetrafluorobenzene ring. When this reagent is treated with an excess of BCl₃, the desired 1,2-bis-(dichloroboryl)tetrafluorobenzene product is observed at early stages of the reaction, but is thermally unstable toward loss of BCl₃ and production of octafluoro-9,10-dichloro-9,10-diboraanthracene, which is the main product of this reaction.¹⁷ Eisch et al. have recently reported a similar condensation reaction involving unfluorinated diborane 1,2-(BCl₂)₂C₆H₄ at elevated temperatures.¹⁸ Evidently, this is a more facile process when the backbone is fluorinated.¹⁹ Fortunately, the reaction of [(C₆F₄)Hg]₃ with BBr₃ produces 1,2-bis-(dibromoboryl)tetrafluorobenzene, with only ~5–10% of the diboraanthracene product

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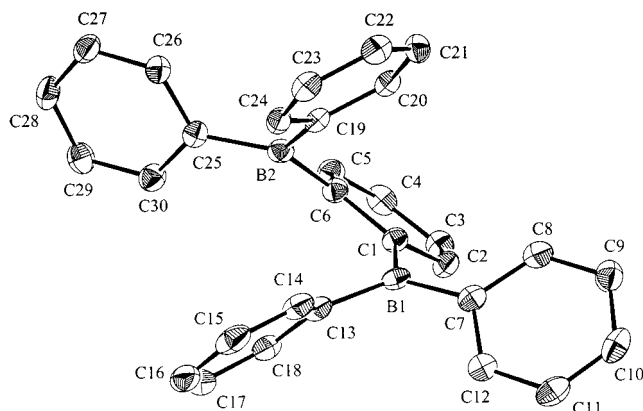
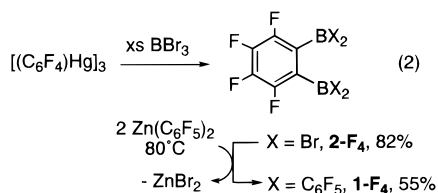


Figure 1. ORTEP diagram of diborane **1-F₄** (50% probability) with the F atoms removed for clarity. Selected bond distances (Å), nonbonded distance (Å), angles (deg) and dihedral angles (deg): B(1)–C(1), 1.568(2); B(1)–C(7), 1.565(2); B(1)–C(13), 1.568(2); B(1)···B(2), 3.138(2); C(7)–B(1)–C(1), 121.72(13); C(7)–B(1)–C(13), 120.00(13); C(1)–B(1)–C(13), 117.55(13); B(1)–C(1)–C(6)–B(2), 19.9(2); C(7)–B(1)–C(1)–C(2), 41.8(2); C(13)–B(1)–C(1)–C(6), 39.8(2); C(19)–B(2)–C(6)–C(1), 39.7(2); C(25)–B(2)–C(6)–C(5), 39.6(2).

in evidence (equation 2); this byproduct is easily removed in



workup. Conversion of 1,2-(BBR₂)₂C₆F₄ to **1-F₄** by using Zn(C₆F₅)₂ proceeds smoothly. It should be noted that attempts to prepare of **1-F₄** directly from [(C₆F₄)Hg]₃ and ClB(C₆F₅)₂^{13,20} were unsuccessful; thus, the use of the zinc reagent to institute the perfluorophenyl groups is essential.

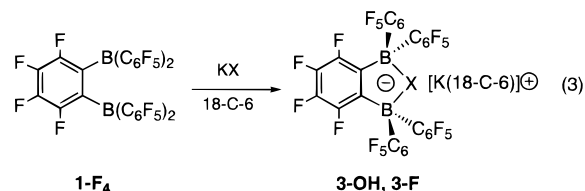
Diborane **1-F₄** crystallizes as a toluene solvate;²¹ a view of its molecular structure (the F atoms and the toluene have been omitted for clarity) is presented in Figure 1 along with selected metrical parameters. Although somewhat distorted from ideal trigonal geometry, the two borane centers are essentially planar ($\Sigma_{\text{C-B-C}} = 359.27(13)$ and $359.67(13)$ for B(1) and B(2),

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(21) Crystal data for **1-F₄**: C₃₀B₂F₂₄·C₇H₈, *M_r* = 938.1; triclinic $\bar{P}1$, *a* = 9.3690(6) Å, *b* = 11.2168(7) Å, *c* = 17.1652(11) Å, α = 99.647(2)°, β = 100.183(2)°, γ = 104.082(2)°, *V* = 1679.70(18) Å³, *Z* = 2, *T* = 160 K, *D_c* = 1.855 g cm⁻³, λ = 0.71073 Å, μ = 0.20 mm⁻¹. Data were collected on a Bruker AXS SMART CCD diffractometer. Refinement on *F*² for all 7835 unique data (19422 measured, *R_{int}* = 0.0255) gave *R_w* = 0.0959 (on *F*²); conventional *R* = 0.0360 on *F* values of 5931 reflections with *F_o*² > 2σ(*F_o*²), difference map within ±0.35 e Å⁻³. Programs were standard control software, SHELXTL (Bruker AXS Inc., Madison, WI, Version 5.1, 1998), and local programs.

respectively) but, as is apparent from this view, the two borane trigonal planes are twisted out of the plane defined by the C₆F₄ backbone by about 39° to avoid unfavorable steric interactions. Furthermore, the two boron centers are tipped out of the C₆F₄ plane (B(1)–C(1)–C(6)–B(2) = 19.9(2)°) to avoid each other.

Despite the intraboron steric crowding, the B(1)···B(2) distance of 3.138(2) Å is enough to accommodate small anions. Indeed, reaction of **1-F₄** with potassium salts of F⁻ and OH⁻ in the presence of 18-crown-6 produces borate anions **3-F** and **3-OH** in which X⁻ is chelated between the two boron centers (equation 3). Chelation of X⁻ is implied by the two equivalent B(C₆F₅)₂



units as indicated by the single (broad) peak observed in the non-temperature dependent ¹¹B NMR spectra (at 14.0 and 2.8 ppm for **3-F** and **3-OH**, respectively) and the sharp, symmetrical ¹⁹F NMR spectra observed at all temperatures (213–313 K) for **3-F**. Furthermore, the upfield shift of the para fluorine resonance relative to the meta signal for the C₆F₅ rings is indicative of a conversion from a neutral borane center to a partially anionic borate center.²² In **3-F**, the μ-F ligand appears as a boron-broadened signal at -167.2 ppm (213 K) in the ¹⁹F NMR spectrum recorded in CH₂Cl₂. At room temperature, this resonance is nearly coincident with the signal due to the meta fluorines of the C₆F₅ rings (-165.0 ppm) but shifts upfield slowly as the temperature is lowered. The origin of the temperature dependence of the chemical shift for this resonance is not clear but, given the lack of coalescence behavior in the rest of the spectrum, we do not believe it is due to a fluxional process in which a nonbridging fluoride ion is exchanging rapidly between boron centers.

Preliminary results suggest that other small anions such as Cl⁻ and MeO⁻ can also be accommodated by **1-F₄**. The incorporation of cations more appropriate for olefin polymerization applications is also feasible, and their use is currently being investigated.

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Supporting Information Available: Experimental and spectroscopic details for **1-H₄**, **1-F₄**, **2-F₄**, **3-F**, and **3-OH**, and tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1-H₄** and **1-F₄** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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