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Perfluorinated Boranes

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Perfluoropentaphenylborole: A New Approach to Lewis Acidic, Electron-Deficient Compounds[**]

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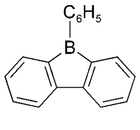
electron-deficient compounds · fluoroaryl boranes · Lewis acids · transmetalation · zirconocene coupling

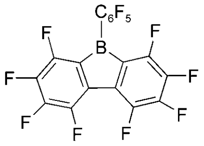
Recent years have witnessed a burgeoning interest in highly Lewis-acidic boron-based compounds, such as perfluoroaryl boranes[1] and boroles, as powerful catalysts for organic synthesis,[1] as co-catalysts for olefin polymerization,[1a,2] and as electron-deficient building blocks for electron-transporting (n-type) materials.[3] While the simplest fluorinated borane, BF_3, has been extensively employed as a Lewis acid in organic chemistry, the introduction of a new class of fluorinated aryl boranes has considerably broadened the scope of applications for boron-based compounds. These developments are directly related to the unique, intrinsic properties of fluorinated aryl boranes, which possess strong Lewis acidity (between those of BF_3 and BCl_3) as well as high thermal and water stability.

The preparation of $B(C_6F_5)_3$, the archetypical perfluoroaryl borane, was initially reported in the 1960s by Stone, Massey, and Park.[4] While the Lewis acidity of $B(C_6F_5)_3$ was recognized at the time, the development of perfluoroaryl borane chemistry remained relatively unexplored until the early 1990s, when the groups of Marks[5] and Ewen[6] recognized the potential of these compounds as activators for olefin polymerization. Their ability to form weakly coordinating anions by abstraction of a methyl group from a metal center has led to reactive cationic metal catalysts that exhibit high polymerization activities. Naturally, $B(C_6F_5)_3$ has also been used as a traditional Lewis acid in a variety of catalytic organic transformations. While many of these reactions follow the traditional mechanism of Lewis acid coordination to the organic functional group, $B(C_6F_5)_3$ has been observed to activate Si–H bonds in the hydrosilylation of ketones.[7] Recently, the pairing of $B(C_6F_5)_3$ with bulky Lewis bases has led to the concept of *frustrated Lewis pairs*[8] and has allowed the unprecedented metal-free activation of small molecules such as H_2.[8,9]

Clearly, the installation of the C_6F_5 group in place of the F atom at the boron center has led to unparalleled reaction chemistry and has triggered the quest for more potent boron-based Lewis acid derivatives. To this end, increasing the fluorine content of the aryl ring with substituents such as perfluorobiphenyl or perfluorobinaphthyl[10] has been an important initial strategy. Meanwhile, boroles **A**–**C** have attracted increasing interest in recent years, not only from a fundamental point of view but also as possible candidates for n-type materials.[3] For example, the synthesis and characterization of dibenzoboroles **A**[11] and **B**[12] has led to the development of potent activators for olefin polymerization and for the construction of electron-accepting building units for n-type materials. Nonannulated boroles (e.g. **C**) represent prime candidates for highly Lewis acidic species and electron-deficient materials, yet the parent borole (C_4H_4BH) remains experimentally unknown owing to its instability and 4π-electron antiaromaticity.[13] However, progress has been made in the preparation and spectroscopic characterization[14] of substituted boroles, and only recently were solid-state structures reported.[15]



A



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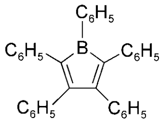

C

The construction of a borole ring with perfluorinated substituents would seem to provide unique access to highly Lewis acidic compounds and electron-deficient materials. This type of structure was first realized with the preparation of the perfluorinated dibenzoborole **B**. The strategy employed is common to that used to access nonfluorinated boroles and relies on a two-step approach: formation of a stannacycle by reaction of a suitable dilithio reagent (dilithiobiphenyl or dilithiobutadiene) with a dichlorostannane and subsequent transmetalation with a boron halide. In contrast, the incorporation of fluorinated moieties around the borole framework presents an unsolved synthetic challenge owing to the intrinsic instability of the key perfluorinated dilithiobutadiene derivative.

Very recently, Piers and co-workers reported a new synthetic route to a perfluorinated pentaphenylborole by transmetalation of a fluorinated stannacycle precursor with-

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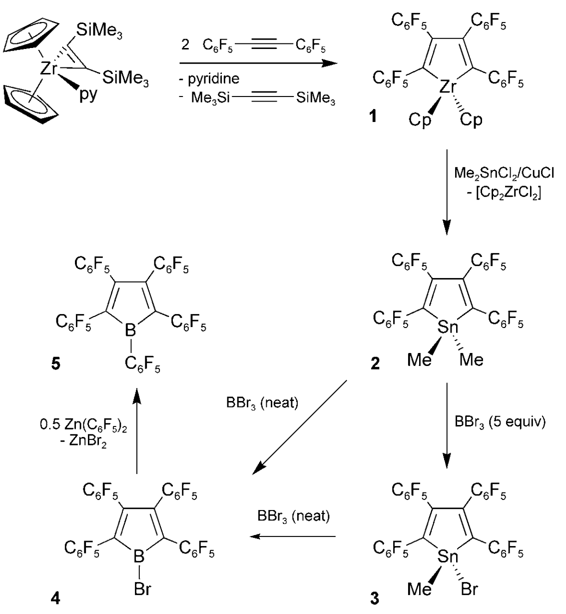
out the involvement of an organolithium intermediate.[16] Their strategy is based on construction of the $C_4(C_6F_5)_4$ framework through the coupling of perfluorophenyl alkynes. The versatility of the reductive coupling of alkynes by zirconocene derivatives, such as Negishi[17] or Rosenthal[18] reagents, has been demonstrated by the synthesis of zirconacyclopentadienes with a variety of substitution patterns. In particular, Tilley and co-workers have shown that the Rosenthal reagent is especially useful for the coupling of fluorinated alkynes.[19] The resultant zirconacyclopentadienes can then be further functionalized by transmetalation reactions involving a wide range of main-group-element halides. The versatility of zirconocene coupling has allowed Piers and co-workers to prepare **1** through the reductive coupling of two equivalents of the fluorinated alkyne $(C_6F_5)CC(C_6F_5)$ with the Rosenthal zirconocene reagent $[Cp_2Zr(py)(Me_3SiCCSiMe_3)]$ (Scheme 1, Cp = C_5H_5, py = pyridine). It is noteworthy that effective alkyne coupling was not achieved when Negishi-type zirconocene reagents were used. Moreover, compound **1** was found to be unreactive in transmetalation attempts with Me_2SnCl_2, $PhBCl_2$, and BBr_3 owing to the reduced nucleophilicity of the Zr–C bonds, a result of the incorporation of pentafluorophenyl groups about the C_4 backbone of the zirconacyclopentadiene. This complication was alleviated with the assistance of CuCl, and transmetalation of **1** with Me_2SnCl_2 was achieved after three days at 80 °C in THF to yield the desired stannacycle **2** in 74 % yield as a crystalline white solid.



Scheme 1. Synthesis of **5** through zirconocene coupling.

While stannanes readily undergo transmetalation reactions with boron halides, the presence of perfluorophenyl groups on the stannacycle **2** again posed difficulties such that treatment of **2** with $ArBX_2$ reagents (X = halide) under forcing conditions did not lead to the generation of a desired borole. Similarly, the reaction of **2** with an excess of BBr_3 in benzene at 80 °C simply led to **3**, resulting from the substitution of only one methyl group at the tin center by bromide. However, when **2** was dissolved in neat BBr_3 and heated to 120 °C for two days, successful transmetalation was achieved, and the bromoborole **4** was isolated in 77 % yield as a red powder. The synthetic feat of preparing the first fully fluorinated pentaaryl borole was finally accomplished by reaction of **4** with the C_6F_5 transfer agent $Zn(C_6F_5)_2$ in toluene at 80 °C after 16 h. The 4π-electron, antiaromatic perfluoropentaphenylborole **5** was isolated as a purple solid in 80 % yield.

The X-ray diffraction analysis of **5** revealed an essentially planar central ring with the C_6F_5 groups organized in a propeller-like arrangement, similar to that observed for nonfluorinated boroles. However, in contrast to nonfluorinated boroles, no close contacts between the boron center and adjacent aromatic groups are present; the molecules are stacked in a staggered conformation as dimers with interdigitated propellers. Surprisingly, the C–C bond lengths of the BC_4 core are similar, which suggests, upon first inspection, delocalization of the 4π-electron system. A similar observation was reported by Braunschweig and co-workers and was rationalized by the involvement of intermolecular boron–phenyl interactions.[15c] However, Yamaguchi and co-workers observed bond alternation in a related system despite the presence of such interactions.[15a] Since boron–phenyl interactions are not present in **5**, Piers and co-workers attribute the similarity in C–C bond lengths to a five-fold disorder rather than to electron delocalization. This conundrum was further probed through a computational analysis of the optimized geometry of **5** in the singlet state, which revealed elongation of B–C and C–C bonds and shortening of C=C bonds compared to the solid-state structure. The calculated singlet–triplet energy gap of 16.9 $\mathrm{kcal\,mol^{-1}}$, with the singlet state being more stable, is slightly larger than that of nonfluorinated pentaaryl boroles (15.4–15.9 $\mathrm{kcal\,mol^{-1}}$).[15a,c]

The UV/Vis spectrum of **5** exhibits a low-energy absorption at 530 nm, characteristic of antiaromatic pentaphenylboroles (λ = 540–605 nm)[14,15c] but blue-shifted owing to the larger HOMO–LUMO gap resulting from fluorination. The antiaromatic character of this compound was further illustrated by the high Lewis acidity of the boron center, such that **5** reacts instantaneously with water. The higher Lewis acidity of **5** compared to $B(C_6F_5)_3$ was also demonstrated through a competition experiment with CH_3CN as the Lewis base, resulting in the exclusive formation of the $CH_3CN{\cdot}$**5** adduct.

The successful synthesis and isolation of the first perfluorinated pentaaryl borole by Piers and co-workers represents a veritable tour de force given the antiaromaticity and tremendous Lewis acidity of these boron-based heterocycles. The synthetic challenge associated with the construction of a BC_4 core decorated with pentafluorophenyl groups stems from the inaccessibility of traditional precursors as well as from the difficulty in overcoming the poor reactivity of the MC_4 core (M = Zr and Sn) in successive transmetalation steps. Piers and co-workers have been able to exploit the synthetic utility of zirconocene coupling reagents for the assembly of the requisite $C_4(C_6F_5)_4$ framework and have managed to develop effective experimental conditions for the synthesis of a borole from a zirconacyclopentadiene.

The versatility of zirconocene coupling presents a unique tool for the preparation of five-membered heterocycles with perfluorinated substituents. The antiaromatic perfluoropentaphenylborole **5** possesses highly desirable properties for both catalysis and materials-based applications. The enhanced Lewis acidity of this compound, compared to more traditional perfluoroboranes, should result in a more potent Lewis acid catalyst for organic transformations and activators for olefin polymerization. Moreover, the highly electron-deficient borole framework should enable the development of efficient n-type conducting materials, in line with the promising results obtained from the less electron-deficient dibenzoborole backbone. While the limited solubility and the moisture sensitivity of this highly reactive compound must be overcome, the tunability of the zirconocene coupling route should allow the introduction of solubilizing groups in a controlled manner by way of the β-directing ability of pentafluorophenyl groups.[19b,c] Moreover, the introduction of suitable functional groups on the alkyne may provide an exciting opportunity to integrate this new class of boroles into extended conjugated systems for the design of electron-deficient n-type conducting materials. On the other hand, introduction of larger substituents at the boron center should afford protection of the vacant p orbital and thus increase the kinetic stability of such reactive compounds. Further development of this area of borole chemistry holds much promise for advances in catalysis and applications of electron-deficient organic materials.

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