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Hydrogen activation with perfluorinated organoboranes: 1,2,3-*tris*(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene

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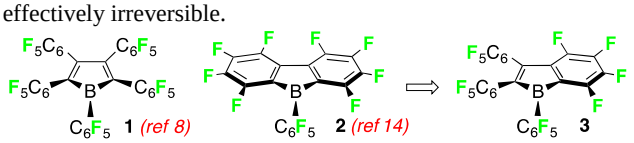
The perfluorinatedboraindene 3 was synthesized and fully characterized. Both computational and crystallographic data show that 3 is antiaromatic. Compound 3 was shown to react reversibly with H_2 and to catalyse the hydrogenation of cyclohexene. The mechanism of catalysis was probed experimentally and computationally.

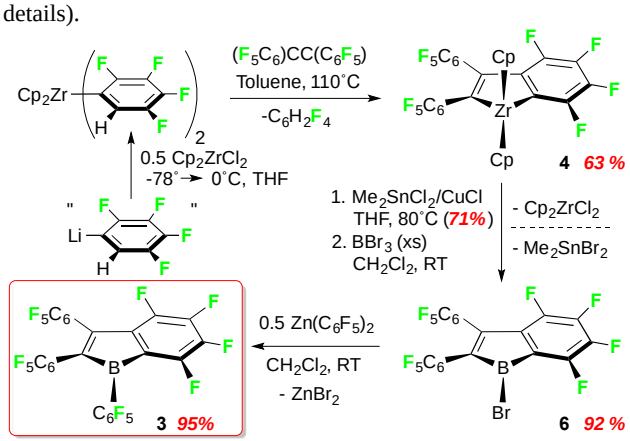
Perfluoroarylboranes are an important class of strong organometallic Lewis acids.[1] Typified by the commercially available and widely employed *tris*-pentafluorophenyl borane, $B(C_6F_5)_3$,[2, 3] applications range from co-catalysts in olefin polymerization processes[4] to Lewis acid catalysis for organic transformations[5] to surface modification in electronic devices.[6] Lately, they have found utility in "metal-free" bond activation processes,[7] in which the borane acts in concert with a suitable Lewis base to heterolytically cleave or activate a wide range of bonds in small molecules. New additions to the family of perfluoroboranes are thus of considerable interest.

We recently reported the synthesis of the highly Lewis acidic perfluoroarylborane **1**,[8] which features an antiaromatic borole core[9] in addition to highly electron-withdrawing fluorinated aryl groups. This compound reacts with a variety of small molecules,[10, 11] including dihydrogen (H_2).[12, 13] In this reaction, dihydrogen is heterolytically cleaved very rapidly by the organoborane alone. Although of fundamental interest, this H_2 activation reaction is of low practical value since the reaction is effectively irreversible.



In this context, we sought other boroles that may also be capable of H_2 activation, but potentially allow for H_2 delivery to a substrate. The strong antiaromaticity of **1** is one reason for the large thermodynamic driving force for its reaction with H_2;[13] we reasoned that tempering this with flanking aromatic rings may be a successful strategy for rendering the reaction with H_2 reversible. Perfluoro-9-phenyl-9-borafluorene[14] **2**, previously prepared in our labs, does not undergo reaction with H_2 under any conditions we have found. Accordingly, we have prepared a conceptual hybrid of **1** and **2**, the perfluoroaryl boraindene **3**. Here we report its synthesis, properties and its reversible reaction with H_2.

The synthesis of **3** was accomplished using a series of transmetalations almost identical to those employed in the synthesis of **1** (Scheme 2).[8] Using known methodology for preparing zirconaindenes,[15] the perfluorinated compound **4** was prepared in good yield by heating $Cp_2Zr(o\text{-}H\text{-}C_6F_4)_2$ in the presence of $(C_6F_5)CC(C_6F_5)$.[16] A subsequent CuCl-mediated transmetalation with dimethyltin dichloride generated the stannaindene **5** (not shown) cleanly, which was isolated and converted to the bromo-boraindene **6** with a large excess of BBr_3. The final step was the transfer of C_6F_5 via $Zn(C_6F_5)_2$[17] to give **3** in very good yield. Note that direct reaction of **4** with BBr_3 did generate **6**, but not very cleanly; the extra step allowed for gram scale syntheses of pure **3**. All compounds were fully characterized, including via X-ray crystallography (see ESI for details).



Scheme 1

Compound **3** is a red crystalline solid that, unlike perfluoropentaphenylborole **1**,[8] is readily soluble in most organic solvents. The ^{19}F NMR spectrum exhibits signals for 13 inequivalent fluorines and a ^{11}B NMR signal at 62 ppm is

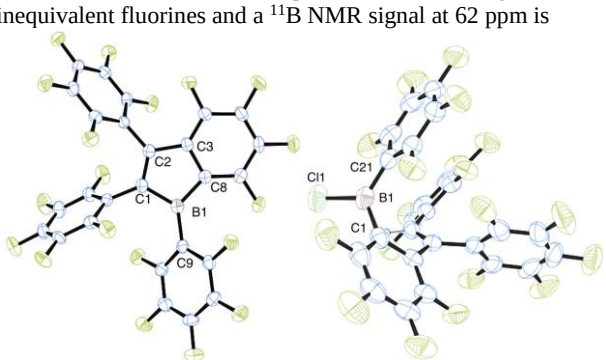


Figure 1: Left: thermal ellipsoid (50%) diagram of **3**. Selected bond lengths (Å) and angles (˚): B1-C1 1.575(5), C1-C2 1.353(5), C2-C3 1.483(5), C3-C8 1.415(5), B1-C8 1.553(6); B1-C1-C2 108.3(3), C1-C2-C3 111.1(3), C2-C3-C8 109.9(3) C3-C8-B1 106.8(3), C8-B1-C1 103.5(3). Right: thermal ellipsoid (50%) diagram of **7**. Selected bond lengths (Å) and angles (˚): C1-B1 1.559(6), C21-B1 1.552(6), Cl1-B1 1.747(4); C21-B1-C1 123.9(3), C21-B1-Cl1 119.0(3), C1-B1-Cl1-117.1(3).

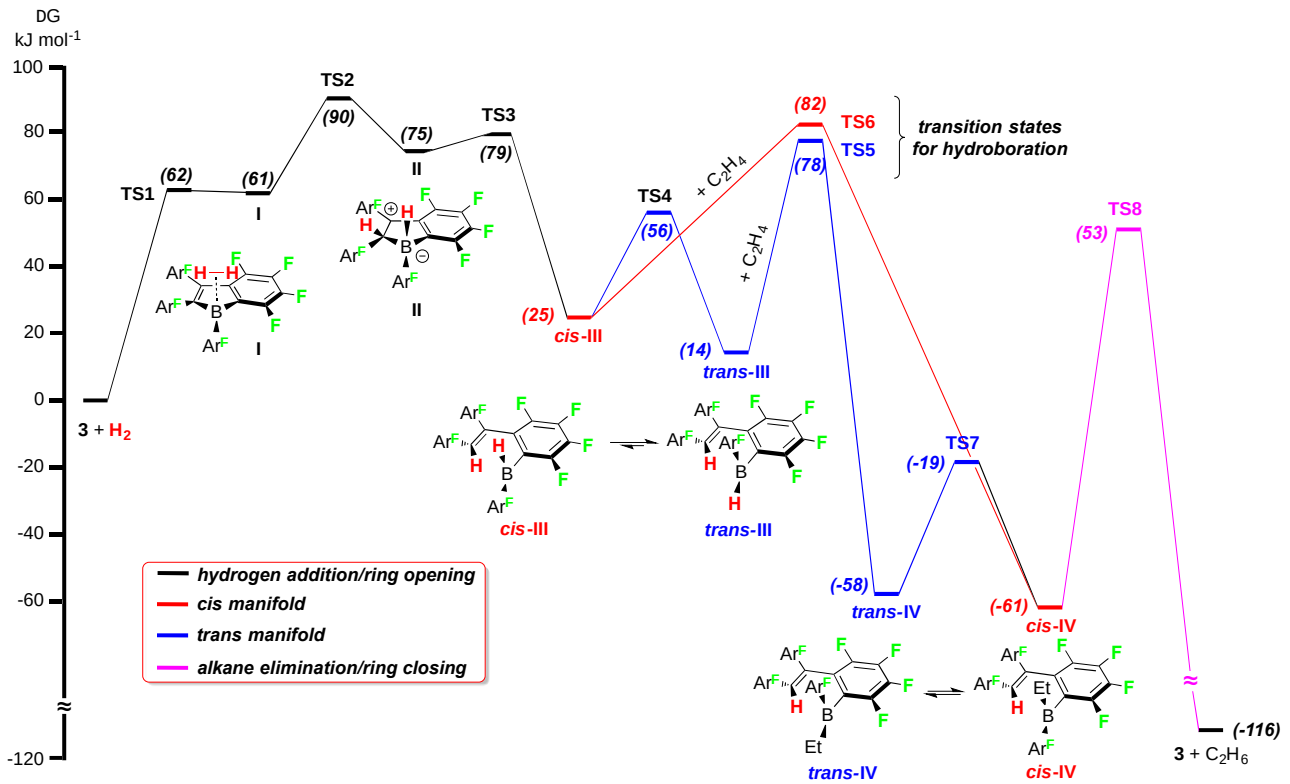
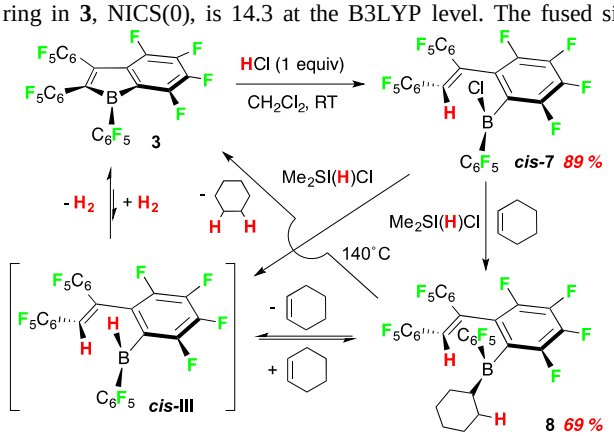


Figure 2: Calculated Gibbs free energies (kJ mol^{-1}; PBE1PBE/TZVP level of theory) for the reaction of 1,2,3-*tris*(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene, **3**, with dihydrogen and the subsequent addition of ethylene and elimination of ethane. See ESI for full details.

intermediate between that of **1**[8] (66 ppm) and **2**[14] (57 ppm). Crystals suitable for X-ray analysis were obtained from hot hexanes, and the structure is shown on the left in Figure 1. The five-membered boracycle is essentially planar, with a sum of internal angles equal to 539.6˚. The bond lengths are indicative of electronic localization, with alternating single-and-double bonds in the five-membered ring. The environment around boron is also planar, with a sum of angles equal to 359.9˚C. As in perfluoropentaphenylborole,[8] the C_6F_5 groups are arranged in a propeller-like array.

The localized bonding in the borole ring of **3** is suggestive of antiaromaticity, a notion supported computationally. The nucleus independent chemical shift at the center of the five membered ring in **3**, NICS(0), is 14.3 at the B3LYP level. The fused six-membered ring proved to be aromatic with a NICS(0) value of -8.5. As with compound **1**, the anti-aromaticity of **3** results in high Lewis acidity. Using the Gutmann-Beckett parameter,[18, 19] we observed a $\Delta\delta$ value of 30.1 ppm for **3** binding Et_3PO in CD_2Cl_2, compared to 26.6 for $B(C_6F_5)$.[20]



Scheme 2

The reaction of boraindene **3** with H_2 was studied experimentally (Scheme 2) and computationally (Figure 2). Based on the chemistry observed for **1**, we anticipated cleavage of a B-C bond to form borane **III**; however, no reaction between **3** and H_2 (ca. 1 atm) was observed at room temperature in toluene-d_8. Upon heating up to 125˚C, a new set of ^{19}F signals began to slowly emerge, but this process was not clean and did not go to completion. While boraindene **3** is itself thermally stable under these conditions, the product of B-C cleavage by H_2 is apparently prone to decomposition at high temperature.

We thus devised a route to generate borane **III** at lower temperatures by preparing the chloroborane **7** via the > 95% selective cleavage of the vinyl B-C bond with one equivalent of HCl. Compound **7** was fully characterized, including by X-ray crystallography (Figure 1, right); we refer to it as the *cis* rotomer because of the cisoid relationship between the Cl and H atoms in this structure. Significantly, treatment of **7** with $Me_2Si(H)Cl$ leads to clean formation of boraindene **3** and H_2 over the course of several hours. Although not detected, borane **III** is strongly implicated as an intermediate by these observed products.

These observations are consistent with the energetic parameters computed for this reaction and summarized on the left part of Figure 2. Unlike the reaction of H_2 with **1**, the addition of H_2 to **3** is moderately endothermic with the calculated $\Delta G_r°$ to ***cis*-III** being 25 kJ mol^{-1}. It is also evident that the initial barrier for H_2 addition (**TS2**, 90 kJ mol^{-1}) is significantly higher than that found previously for the analogous reaction involving **1** (61 kJ mol^{-1}).[13] Hence, the thermodynamics favour **3** and H_2 over **III**. As in the reaction manifold for borole **1**, the equilibrium between

rotomers of **III** is characterized by a reasonably high barrier, and cyclization/H_2 elimination to reform **3** can only occur from ***cis*-III**. Finally, we also note that the addition of H_2 can involve either one of the two intraring B-C bonds of **3**, the transition state for the alternative pathway (**TS2b**) being only 7 kJ mol^{-1} higher in energy than **TS2** (see ESI). The product from this reaction, ***cis*-IIIb**, is energetically on par with ***cis*-III** (24 vs. 25 kJ mol^{-1}).

Having established the viability of borane intermediate **III**, we reasoned that it might be trapped by an olefin substrate via hydroboration;[21, 22] elimination of alkane instead of H_2 from such an alkylborane product would close a catalytic cycle. Computations on the model olefin ethylene showed this to be strongly exothermic (Figure 2, right side), albeit with a rather high barrier for alkane elimination of 114 kJ mol^{-1}. Still, the transition state for elimination (**TS8**) is well below the highest energy point on the surface (**TS2**) and the transition states for retrohydroboration (**TS5** and **TS6**). For experimental studies, cyclohexene was chosen as a substrate. As shown in Scheme 2, treatment of **7** with silane in the presence of cyclohexene leads smoothly to the expected hydroboration product **8**, which was isolated in 69% yield and characterized by NMR spectroscopy and elemental analysis. Significantly, heating solutions of **8** to 140˚C leads to elimination of both cyclohexene and cyclohexane, (formed in an ≈ 6:1 ratio) and formation of **3** along with other species (Figures S17 and S18). This indicates that elimination of alkane from **8** is operative, but that retrohydroboration[22] is strongly competitive (indeed favored) for this substrate, an observation consistent with the detectable amount of H_2 also produced (Figure S17).

Although the above discussion illustrates the potential for **3** to serve as a hydrogenation catalyst for olefins, attempts to catalytically hydrogenate cyclohexene using **3** met with only modest success. Using 10 or 20% loadings of **3**, approximately 4-5 turnovers for cyclohexene hydrogenation was observed at 140˚C in C_6D_6 under ≈ 5 atm of H_2. At the lower catalyst loading, the NMR spectral yield of cyclohexane was 54% with about 30% of the cyclohexene unreacted. Complete consumption of cyclohexene was observed at the 20% loading but the yield of cyclohexane was only 70%. A separate experiment in which **3** is heated to 140˚C with cyclohexene in the absence of H_2 shows that a reaction to an uncharacterized product occurs within 90 minutes; this accounts for most of the missing cyclohexene/cyclohexane. The resonances for this product can also be found in the ^{19}F NMR spectrum resulting from the heating of **8** at this temperature (see Figure S18). Presumably, retrohydroboration leads to **3** and cyclohexene, which react to form this as yet uncharacterized species.

While the catalytic cycle involving ring opening/hydroboration/ring closing is demonstrably viable, it is also possible that the alkyl borane **8** reacts directly with H_2 to liberate alkane in a σ bond metathesis reaction[23] reminiscent of what was proposed for the hydrogenation of various olefins using *bis*-pentafluorophenylborane ($HB(C_6F_5)_2$,[21] Piers' borane).[24] We cannot eliminate this possibility at this stage, but note that the computed energies for the transition states for the reaction of H_2 with ***cis*-IV** and ***trans*-IV** (to eliminate ethane and generate **III**) lie at 65 and 71 kJ mol^{-1}, respectively, on the energy scale of Figure 2 (**TS9** and **TS10**, see ESI). Thus, the bimolecular σ bond metathesis reaction faces a higher barrier than unimoleculer direct elimination of alkane, but is likely a competitive pathway for alkane liberation.

In summary, we report here the synthesis of a new perfluorinated organoborane, the triphenylboraindene **3** and show both experimentally and computationally that its reaction with H_2 is reversible and endergonic. Consequently, and in contrast to the related borole **1**, H_2 addition is reversible and a pathway for delivery of H_2 to the olefinic substrate cyclohexene has been identified. We have experimental and computational evidence that a novel ring-opening/ring-closing sequence for the hydrogenation of cyclohexene is viable, but side reactions of substrate with catalyst limit the turnovers of the reaction; alternate paths[24] are also plausible. Substrate scope using **3** is somewhat limited by its reactivity towards olefinic functions in the absence of H_2, and so modifications to the structure of **3** to improve catalyst performance are underway. Nevertheless, the current work demonstrates a novel catalytic path for metal-free olefin hydrogenation.

Notes and references

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