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# Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane, a Partially Fluorinated Boron Lewis Acid with Fluorination Distal to the Boron Atom

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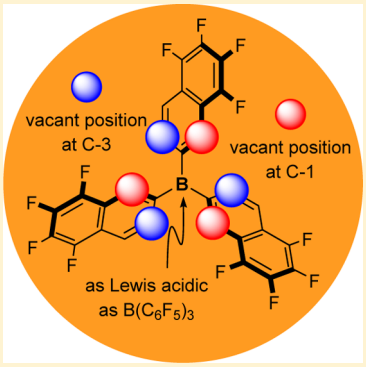
Supporting Information

**ABSTRACT:** Typical congeners of the boron Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, are fluorinated at the aryl groups directly attached to the boron atom. The chemistry of related electron-deficient boranes with fluorination distal to the Lewis acidic center is largely unexplored. The preparation and characterization of tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane are reported. It serves as a model system that provides sites for further substitution at C-1 and C-3 of the naphthalen-2-yl units. A Gutmann–Beckett analysis of its Lewis acidity revealed that, despite remote fluorination, it is as Lewis acidic as $B(C_6F_5)_3$. The new Lewis acid performs equally well in C=O and C=N reduction as well as dehydrogenative Si–O coupling involving Si–H bond activation. Adducts with water and a phosphine oxide are crystallographically characterized.




The role of electron-deficient boranes decorated with fluorinated aryl substituents in frustrated Lewis pair (FLP) chemistry recently brought them back into focus.[1] The archetypical member of these boron Lewis acids, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$, **1**],[2] had previously gained prominence as a cocatalyst in metallocene-mediated polymerization processes[3] and in catalytic Si–H bond activation.[4] The development of new analogues of **1** with different aryl groups and degrees of fluorination[5] is hence relevant to several areas of synthetic chemistry.

Our laboratory is particularly involved in the design of chiral congeners of **1**, and we introduced (*S*)-**2**·THF with a 1,1′-binaphthalene-2,2′-diyl backbone (Figure 1, upper left).[6] Liu and Du recently reported the related system (*S*)-**3** with additional substitution in the 3,3′ positions (Figure 1, upper right).[7] The boron atom in (*S*)-**2**·THF and (*S*)-**3** is, however, not directly attached to the chiral fragment and, accordingly, relatively remote from its chiral axis. Conversely, Piers and co-workers had prepared (*R*)-**4** where one of the $C_6F_5$ groups in **1** is replaced by a nonfluorinated 1,1′-binaphthalene-2-yl unit (Figure 1, lower left).[8] Congeners of **1** based on that chiral element but devoid of $C_6F_5$ groups have not been described yet. To retain high Lewis acidity in such systems, partial if not perfluorination of the 1,1′-binaphthalene-2-yl group will be vital. The fully fluorinated *β*-naphthyl $B(C_{10}F_7)_3$[9] is known (not shown) but does not serve as a model compound for the above purpose. In turn, unprecedented **5**,[10] with 5,6,7,8-tetrafluoronaphthalen-2-yl units, would be suitable, though, as C-1 would still be available for its connection to another naphthalen-2-yl unit and vacant C-3 would allow for the installation of a further substituent (Figure 1, lower right). On the downside, fluorination would be distal from the boron atom, and the present investigation is meant to see whether remote fluorination as in **5** is detrimental to the Lewis acidity of the boron atom relative to **1**. We report here the preparation and characterization of tris(5,6,7,8-tetrafluoronaphthalen-2-yl)-borane (**5**) as well as its application in typical reactions involving Si–H bond activation.

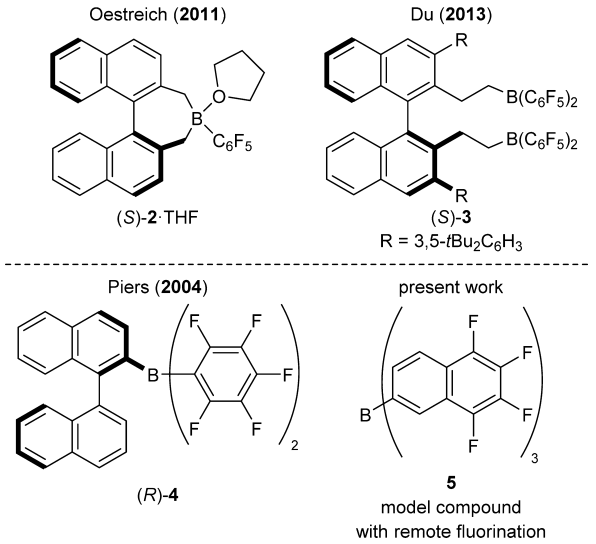



**Figure 1.** Chiral $C_6F_5$-substituted boranes (upper) and congeners of **1** with naphthalen-2-yl groups (lower).

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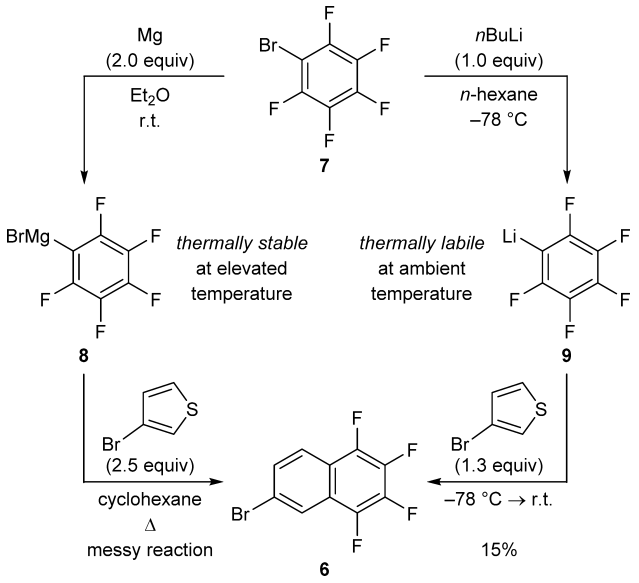
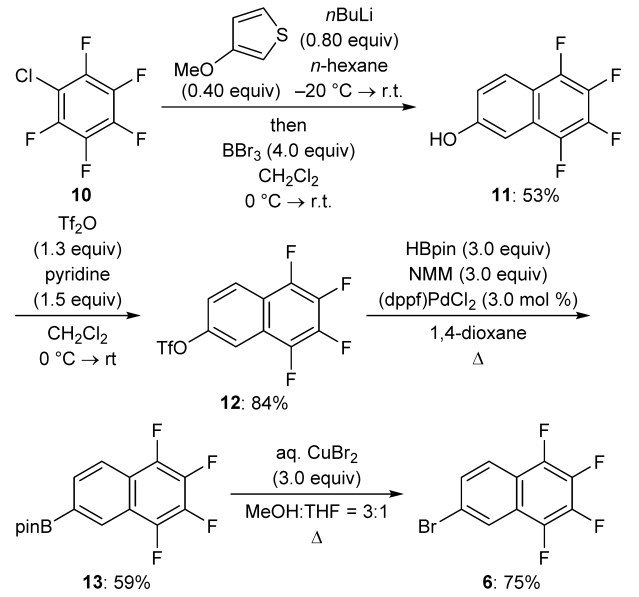
We anticipated that the title compound **5** would emerge from the corresponding halide, e.g., bromide **6** (Schemes 1 and 2). The plan was to transform **6** into a nucleophile by a halogen−metal exchange reaction followed by electrophilic substitution with $BX_3$ (X = leaving group). A straightforward one-step procedure toward **6** from $C_6F_5Br$ (**7**) via the thermally robust Grignard reagent **8** had been reported but produced **6** as an inseparable mixture with byproducts in our hands (**7** → **8** → **6**, Scheme 1, left).[11] We decided to test the same route via the fragile lithium compound **9**, an aryne precursor that rapidly undergoes *β*-elimination of lithium fluoride at temperatures above −78 °C (***Explosion!***).[2b] **7** was, therefore, metalated at −78 °C and allowed to warm to room temperature in the presence of the diene overnight (**7** → **9** → **6**, Scheme 1, right). This setup indeed afforded analytically pure **6** yet in rather low isolated yield.

**Scheme 1. One-Pot Approaches to Key Intermediate 6: 6-Bromo-1,2,3,4-tetrafluoronaphthalene**




**Scheme 2. Five-Step Approach to Key Intermediate 6: 6-Bromo-1,2,3,4-tetrafluoronaphthalene**

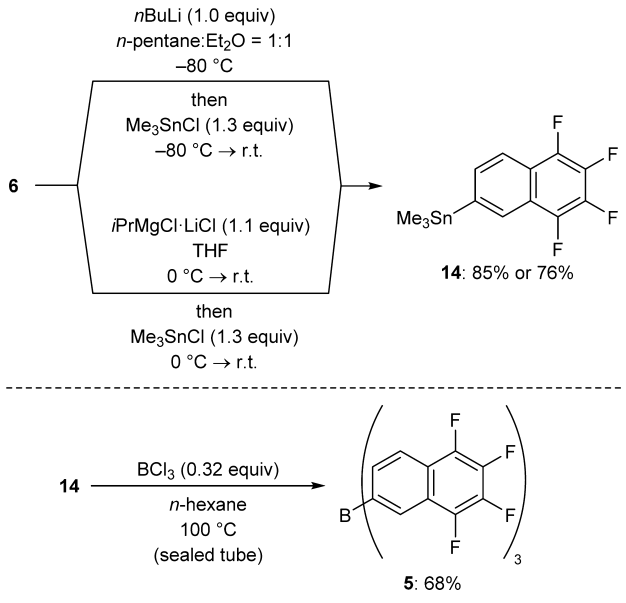



The limited success with the above direct approaches to building block **6** prompted us to investigate a three-step sequence starting from literature-known *β*-naphthol **11**[12] (Scheme 2). $C_6F_5Cl$ (**10**) was engaged in a similar Diels−Alder reaction as before, and the hydroxy group was liberated from the methyl ether by conventional treatment with $BBr_3$ (**10** → **11**). Triflation of **11** and subsequent coupling with pinacol borane furnished **13** in acceptable yield on a half-gram scale (**11** → **12** → **13**). The original procedure of the borylation[13] was modified to repress defunctionalization; *N*-methylmorpholine (NMM) instead of triethylamine[14] increased the ratio of **13** to 1,2,3,4-tetrafluoronaphthalene from 62:48 to 77:23. After treatment of **13** with aqueous copper(II) bromide (**13** → **6**),[15] we arrived at 6-bromo-1,2,3,4-tetrafluoronaphthalene (**6**) in 20% overall yield over five steps.

With key intermediate **6** in hand, we attempted to prepare borane **5** via bromine−lithium exchange with *n*BuLi followed by rapid addition of $BCl_3$, a strategy commonly used in the preparation of $B(C_6F_5)_3$ (**1**). Unfortunately, this obvious approach proved to be difficult. At temperatures above −78 °C and in polar solvents, nucleophilic substitution of fluorine atoms in **6** became a competing pathway, even with bulkier *t*BuLi. Lithiation in nonpolar solvents was too slow to be practical. After extensive optimization, we found that a mixture of *n*-pentane and $Et_2O$ enabled the lithiation of **6**, but reaction with $BCl_3$ resulted in the corresponding borate rather than borane **5** (not shown). An alternative route consisting of successive bromine−magnesium exchange using Knochel's *i*PrMgCl·LiCl[16] and addition of $BF_3{\cdot}OEt_2$ also failed to give desired **5** (not shown).

Since the direct electrophilic substitution of metalated **6** with boron electrophiles failed, we revised our strategy and reacted the metalated intermediate with $Me_3SnCl$ (**6** → **14**, Scheme 3, upper). Isolated yields were equally high for both the lithiation and the magnesation methods. Gratifyingly, transmetalation

**Scheme 3. Preparation of Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane (5)**





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from tin to boron[17] allowed for the conversion of stannane **14** into borane **5** (**14** → **5**, Scheme 3, lower). Typical purification of crude **5** by sublimation proved to be impossible due to the high temperatures (200 °C) required for that molecular weight. The carbon−boron bonds in **5** were too labile, and 1,2,3,4-tetrafluoronaphthalene was detected by NMR spectroscopy. However, pure **5** was obtained by precipitation from a solution in 1,2-difluorobenzene (**5** showed low solubility in common noncoordinating solvents). Cleavage of the carbon−boron bond(s) in **5** was also observed when exposed to traces of moisture, while $B(C_6F_5)_3$ (**1**) forms stable adducts with water.[18] We were therefore delighted to find that **5** crystallized from wet THF as $\mathbf{5}{\cdot}OH_2(THF)_2$ along with two molecules of THF forming hydrogen bridges with the acidified hydrogen atoms of the borane-coordinated water molecule (Figure 2).

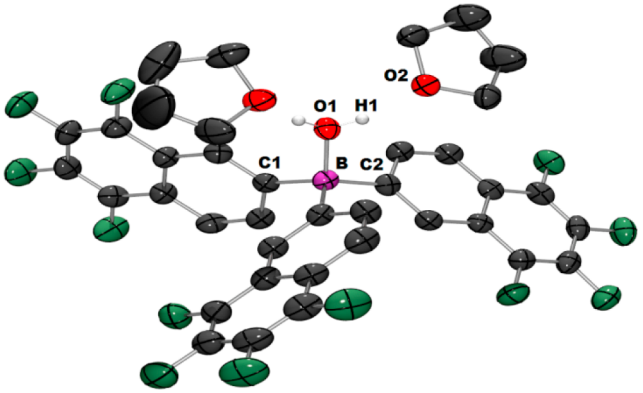



**Figure 2.** ORTEP representation of $\mathbf{5}{\cdot}OH_2(THF)_2$, rendered with POV-Ray. Selected bond lengths [Å] and angles [deg]: B−O1 1.583(5), B−C1 1.614(6), O1−H1 0.82(5), H1−O2 approximately 1.71, C1−B−C2 111.9(3), C1−B−O1 105.9(3).

The new motif of **5** distinguishes itself from those of known electron-deficient triarylboranes by fluorination distal and no fluorination promixal to the boron atom. We asked ourselves to what extent the Lewis acidity is diminished by this remote fluorination. As for (*S*)-**2**·THF,[6a] we decided to make use of the Gutmann−Beckett method[19,20] as a measure of the Lewis acidity relative to $B(C_6F_5)_3$ (**1**). For this, we determined the $\Delta\delta$ values of the $^{31}P$ NMR chemical shifts of free $Et_3PO$ and its Lewis acid/base adducts with **5** and **1** in $CD_2Cl_2$ and $C_6D_6$ at room temperature (Table 1).[21] We were surprised to see that the $\Delta\delta$ values obtained for $\mathbf{5}{\cdot}Et_3PO$ and $\mathbf{1}{\cdot}Et_3PO$ were nearly identical, indicating that **5** is as strong a Lewis acid as **1** relative to $Et_3PO$. Cognate $\mathbf{5}{\cdot}Ph_3PO$ was also crystallograhically characterized (Figure 3). Its molecular structure showed a B−O distance longer than that in $\mathbf{1}{\cdot}Ph_3PO$[19b] [1.583(3) Å versus 1.538(3) Å] but the B−O−P linkage was found to be bent [144.52(13)° for $\mathbf{5}{\cdot}Ph_3PO$] rather than linear [178.7(2)° for $\mathbf{1}{\cdot}Ph_3PO$].

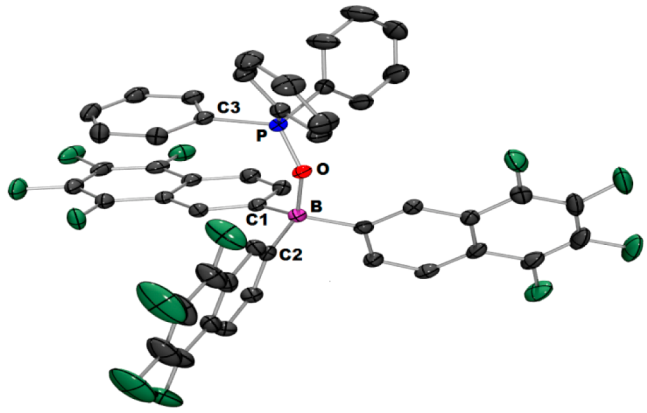
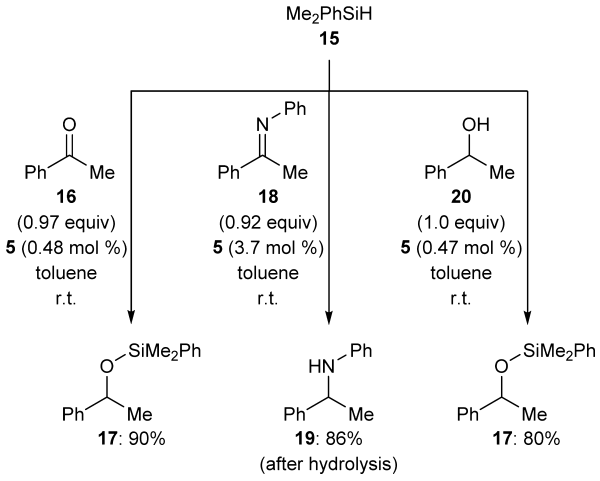



**Figure 3.** ORTEP representation of $\mathbf{5}{\cdot}Ph_3PO$, rendered with POV-Ray. Selected bond lengths [Å] and angles [deg]: B−C1 1.632(3), B−O 1.583(3), O−P 1.5174(14), C1−B−C2 111.90(17), C1−B−O 108.63(16), B−O−P 144.52(13), O−P−C3 114.16(9).

Encouraged by the above findings, we probed the catalytic activity of **5** in typical reactions involving Si−H bond activation (Scheme 4). Using hydrosilane **15**, C=O[4a] and C=N[4c]

**Scheme 4. Typical Reactions Involving Si−H Bond Activation to Probe the Catalytic Activity of Borane 5**




reduction worked equally well (**16** → **17** and **18** →**19**). Also, dehydrogenative Si−O coupling[4b] was efficiently catalyzed by **5** (**20** → **17**). The carbonyl reduction and the Si−O coupling could be performed in good isolated yields at low catalyst loadings (<0.5 mol %) within two hours. As expected, the imine reduction required a higher catalyst loading and a longer reaction time. These results compare well with those obtained with **1**.

In conclusion, we accomplished the synthesis of a novel electron-deficient borane that bears partially fluorinated naphthalen-2-yl groups. Although these substitutents lack

**Table 1. Gutmann−Beckett Analysis: Determining the Lewis Acidity of 5 Relative to 1**[a,b]

| NMR solvent | $^{31}P\{^1H\}$ NMR ($\delta$/ppm) $Et_3PO$ | $^{31}P\{^1H\}$ NMR ($\delta$/ppm) $\mathbf{5}{\cdot}Et_3PO$ | $^{31}P\{^1H\}$ NMR ($\delta$/ppm) $\mathbf{1}{\cdot}Et_3PO$ | relative Lewis Acidity (%)[c] |
|---|---|---|---|---|
| $C_6D_6$ | 45.3 | 74.7 ($\Delta\delta$ = 29.4) | 75.3 ($\Delta\delta$ = 30.0) | 98 |
| $CD_2Cl_2$ | 50.3 | 76.6 ($\Delta\delta$ = 26.3) | 76.9 ($\Delta\delta$ = 26.6) | 99 |

[a]0.020−0.025 M solutions in the indicated solvent at room temperature. [b]$\Delta\delta$ values relative to free $Et_3PO$. [c]Calculated from ($\Delta\delta$ for **5**)/($\Delta\delta$ for **1**) × 100.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fluorination promixal to the boron atom, Lewis acid **5** shows hardly any difference in Lewis acidity to often-used $B(C_6F_5)_3$ (**1**). Moreover, **5** performs equally well in catalytic Si−H bond activation. With the C-1 and C-3 positions in the naphthalen-2-yl backbone available for further functionalization, these results might pave the way for the preparation of chiral boranes with remotely fluorinated 1,1′-binaphthalene-2,2′-diyl backbones.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, characterization data, NMR spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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