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Interactions of C-F bonds with hydridoboranes: Reduction, Borylation and Friedel-Crafts Alkylation

Karlee L. Bamford,[a] Saurabh S. Chitnis,[a] Zheng-wang Qu,[b]* and Douglas W. Stephan*[a]

Dedication ((optional))

Abstract: The stoichiometric reactions of the alkylfluorides 1-fluoroadamantane (Ad-F), fluorocyclohexane (Cy-F), 1-fluoropentane (Pent-F) and benzyl fluorides with secondary boranes pinacolborane (HBpin), catecholborane (HBcat), 9-borabicyclo(3.3.1)nonane (9-BBN) and Pier's borane ($HB(C_6F_5)_2$) are described. While HBcat, 9-BBN and $HB(C_6F_5)_2$ reduce Ad-F to Ad-H, the latter borane was shown to react with secondary and primary fluoroalkanes, affording C-F borylation, while benzyl fluorides undergo Friedel-Crafts chemistry.

The activation of carbon-fluorine (C-F) bonds is challenging as they are the strongest single bond involving carbon (536 kJ/mol).[1] While the stability of C-F bonds has been advantageous for use in agrochemicals[2] and pharmaceuticals,[2c, 3] strategies to effect subsequent transformations C-F bonds are quite limited. Transition metal systems have been shown to preferentially react with C(sp^2)-F bonds,[4] while proton-mediated Friedel-Crafts reactions of polyaromatic monofluoro-arenes and benzyl fluorides have been described by Siegel[5] and Paquin et al.,[6] respectively. More recently a number of studies have described the activation of C(sp^3)-F bonds by interaction with the low energy LUMOs (p-orbital) of main group electrophiles.[7] For example, hydrodefluorination has been well documented for a variety of silylium and disilyl cations.[8] Similarly, stoichiometric alkylation of the CF_3 functional group has been effected using aluminum alkyl species,[9] an alumenium cation[10] or aluminum-chlorofluoride species.[11]

In 2013, we developed the electrophilic phosphonium cation (EPC), $[(C_6F_5)_3PF][B(C_6F_5)_4]$[12] in which the Lewis acidity is derived from the σ*-orbital. This EPC is an effective catalyst for the hydrodefluorination of fluoroalkanes and was subsequently employed to mediate Friedel-Crafts alkylation of arenes using alkyl-CF_3 and benzyl fluoride substrates. In a related sense, Gabbaï and coworkers[13] developed the air-stable species $[(C_6F_5)_4Sb][B(C_6F_5)_4]$ for hydrodefluorination catalysis. In further related work, Greb[14] has developed the silicon-based species $[Si(O_2C_6Cl_4)_2]$, which becomes hypervalent in exhibiting its affinity for fluoride. In very recent work, we have extended such C-F bond hydrodefluorination catalysis to the P(III) coordination compounds, $[(bipy)PPh][B(C_6F_5)_4]$ and $[(terpy)PPh][B(C_6F_5)_4]$ (bipy = 2,2'-bipyridine, terpy = 2,2':6',2"-terpyridine).[15]

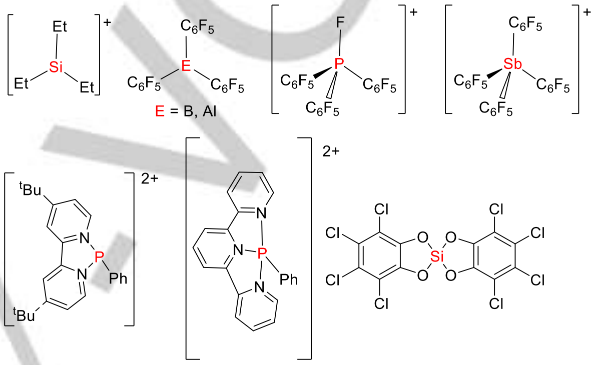

Figure 1. Selected main group systems that react with C-F bonds.

The possibility of borane-mediated C-F bond activation was first revealed in 1943[16] with the use of BF_3 and was furthered in the seminal work of Olah.[17] The use of Et_3NBF_3 in dehydrofluorination reactions was later described by Knunyants[18] in 1975. N-heterocyclic carbene-borane adducts have also been shown to affect haloalkane C-X (X = Cl, Br, I) bond reduction, albeit under forcing conditions (140 °C), although this reactivity was not extended to C-F bonds.[19] In 2012, we reported the use of the Lewis acid, $B(C_6F_5)_3$[20] for hydrodefluorination of fluoroalkanes. Despite these findings, the fundamental reactivity of hydridoboranes with C(sp^3)-F bonds has not been explored.[21] Herein, we report the facile reactions of hydridoboranes with a representative set of fluorinated organic substrates, demonstrating the ability of these readily accessible reagents to effect stoichiometric reduction, borylation or Friedel-Crafts reactivity of C-F bonds.

In initially probing stoichiometric C-F reduction using hydridoboranes, pinacolborane (HBpin) was combined with 1-fluoroadamantane (Ad-F), fluorocyclohexane (Cy-F), or 1-fluoropentane (Pent-F) in CD_2Cl_2 in J-Young NMR tubes. In all cases, HBpin was unreactive at ambient temperature or upon heating to 55-80 °C. In contrast, the tertiary fluoride, Ad-F and catecholborane (HBcat) reacted at ambient temperature in < 10 mins, affording adamantane and FBcat as the major products as evidenced by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy. The similar conversion of Ad-F to adamantane was observed for the reaction with 9-borabicyclo(3.3.1)nonane (9-BBN), although this required 24 h at ambient temperature. In the case of Pier's borane, $HB(C_6F_5)_2$, ^{11}B NMR spectroscopy showed resonances at 43.2 and 22.2 ppm attributable to the species $FB(C_6F_5)_2$ and $F_2B(C_6F_5)$, respectively. This was confirmed by the independent generation of $FB(C_6F_5)_2$ and $F_2B(C_6F_5)$ from $HB(C_6F_5)_2$ and SbF_3 following

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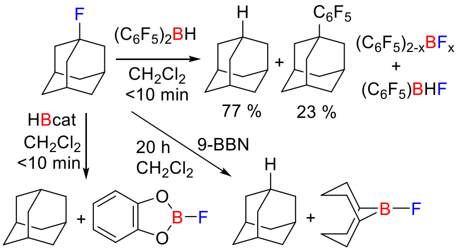
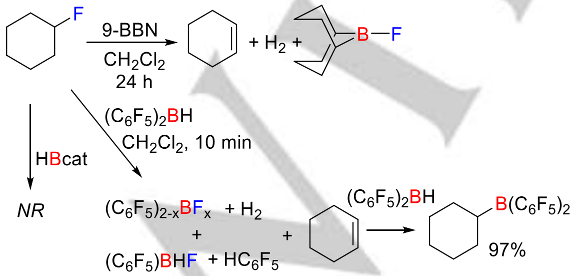
the method of Chambers and Chivers.[22] Monitoring by ^1H, ^{11}B, and ^{19}F NMR spectroscopy revealed $HB(C_6F_5)_2$ reacts with Ad-F at ambient temperatures to give the rapid formation of adamantane and C_6F_5-adamantyl in a 77:23 ratio. These observations are consistent with a mechanism involving coordination of the Ad-F to borane prompting F/H or F/C_6F_5 metathesis in processes that are apparently competitive.



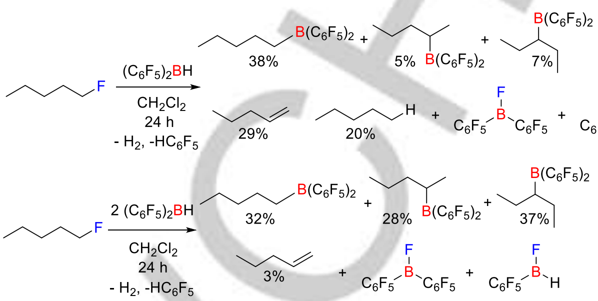
Scheme 1 Reactions of hydridoboranes with Ad-F (x = 1 or 2).

The secondary fluoride Cy-F was unreactive with HBcat at ambient temperature, whereas it reacted quantitatively with 9-BBN over 24 h at ambient temperature, effecting the formation of cyclohexene, H_2 and 9-F-9-BBN. In a similar, albeit considerably faster reaction, Cy-F and $HB(C_6F_5)_2$ reacted yielding $CyB(C_6F_5)_2$ as the dominant product. While treatment of Cy-F with one equivalent of $HB(C_6F_5)_2$ afforded a mixture of cyclohexene, cyclohexane and $CyB(C_6F_5)_2$, the use of two equivalents of $HB(C_6F_5)_2$, afforded $CyB(C_6F_5)_2$ in 97% yield with a 3 % yield of cyclohexane. The former product results from the hydroboration of cyclohexene and gives rise to the characteristic resonance at 73.1 ppm by ^{11}B NMR spectroscopy.[23] These observations suggest an initial borane-fluoroalkane interaction that prompts defluorination with concurrent loss of H_2. This is consistent with the increased acidity of the proton on the β-carbon and the observed deprotonation product, cyclohexene. It is noteworthy that no evidence of cyclohexyl-cation rearrangement to methylcyclopentene was observed, inferring that either dehydrofluorination is a concerted process or that deprotonation of the cyclohexyl-cation by $[HBF(C_6F_5)_2]^-$ is fast relative to carbocation rearrangement. Regardless, the formation of $CyB(C_6F_5)_2$ provides a rare, if not unprecedented, example of uncatalyzed C-F borylation and stands in marked contrast to the hydrodefluorination chemistry observed for reactions of hydridoalanes and fluoroalkanes.[24]



Scheme 2 Reactions of hydridoboranes with Cy-F (x = 1 or 2).

The corresponding reactions of $HB(C_6F_5)_2$ with chloro-, bromo- and iodo-cyclohexanes showed no reaction at ambient conditions. Indeed, a competition experiment using a 1:1:1:1 mixture of Cy-X (X = F, Cl, Br, I) with $HB(C_6F_5)_2$ (2 equivalents) revealed the consumption of only the Cy-F substrate (See ESI) after 10 minutes. This preferential cleavage of C-F bonds demonstrates reactivity that is orthogonal to that of traditional metal-derived systems where reactions are selective to C-X (X = Cl, Br, I) bonds.



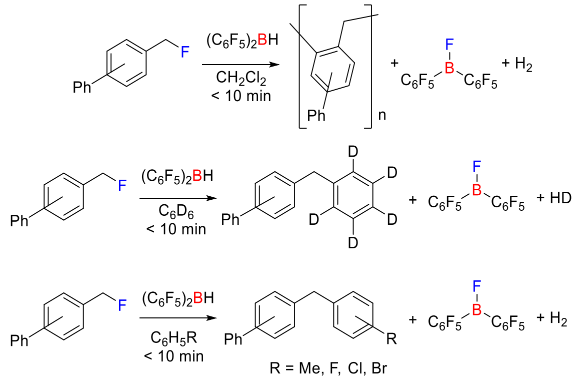
Scheme 3 Reactions of boranes with Pent-F.

The primary alkyl fluoride Pent-F was unreactive with HBpin, HBcat and 9-BBN while it reacted with $HB(C_6F_5)_2$ over 24 h at ambient temperature. ^1H, ^{11}B, and ^{19}F NMR spectroscopy were consistent with the formation of H_2 and a mixture of five new boron-containing species exhibiting ^{11}B chemical shifts at 75.7, 59.4, 52.4, 43.2 and 22.2 ppm. The first three resonances were attributed to the products of $HB(C_6F_5)_2$ hydroboration of 1-pentene and 2-pentene,[25] while the latter two resonances arise from $FB(C_6F_5)_2$ and $F_2B(C_6F_5)$, respectively. Performing the reaction with two equivalents of borane provide the isomeric hydroboration products in 32%, 28% and 37% yields, respectively (Scheme 3). These observations are consistent with dehydrofluorination and subsequent hydroboration, analogous to the C-F borylation observed with Cy-F. While the formation of an isomeric mixture of pentenes could suggest the intermediacy of a primary carbocation, retrohydroboration is also a viable explanation.[26]

Substrates in which β-hydrogen atoms are absent were also examined. To this end, the reactions of the benzyl fluorides p-$PhC_6H_4CH_2F$ or o-$PhC_6H_4CH_2F$ with hydridoboranes were also probed in CH_2Cl_2. For 9-BBN, monitoring the reaction mixtures by ^{19}F NMR spectroscopy confirmed the formation of 9-F-9-BBN, while broadened signals in ^1H NMR spectra (3.80-4.00 ppm) were consistent with the formation of oligomeric poly(arylmethylenes). This interpretation was supported by mass spectroscopic data showing low molecular weight oligomeric species (m/z < 1200, see ESI). Vigorous bubbling of reaction mixtures was confirmed to be the result of H_2 loss by ^1H NMR spectroscopy. Collectively, these observations are reminiscent of the BF_3-catalyzed alkylation of benzene using fluoroalkanes that was previously described by Olah.[27] A similar oligomerization result was obtained using the borane $HB(C_6F_5)_2$.

The formation of oligomeric products strongly suggests that fluoride abstraction prompts the transient generation of a benzyl carbocation which then undergoes Friedel-Crafts benzylation of unreacted benzyl fluoride with the subsequent liberation of H_2. To further support this notion, the reactions of $HB(C_6F_5)_2$ with *o*- and *p*-$PhC_6H_4CH_2F$ were repeated in an arene (C_6D_6) solvent. In this case, the Friedel-Crafts alkylation of the solvent was seen affording selectively the respective products o- and p-$PhC_6H_4CH_2(C_6D_5)$, as evidenced by NMR spectroscopy (See ESI).

The analogous reaction using 9-BBN yields the respective products *o*- and *p*-$PhC_6H_4CH_2(C_6D_5)$, however the reaction takes considerably longer, 3 or 36 hours, respectively. The benzylations of toluene, fluorobenzene, chlorobenzene and bromobenzene affording *p*-$PhC_6H_4CH_2(C_6H_4R)$ (R = Me, F, Cl Br) were also achieved quantitatively using $HB(C_6F_5)_2$, with the formation of two substitutional isomers (*ortho, para*) in each case, under similar conditions in neat arene (See ESI).



Scheme 4 Reactions of boranes with o- or p-$PhC_6H_4CH_2F$.

Efforts to activate C-F bonds of polyfluorinated substrates were also undertaken. Reactions of 9-BBN or $HB(C_6F_5)_2$ with α,α,α-trifluorotoluene, (trifluoromethyl)cyclohexane, 2H,3H-decafluoropentane or octadecafluorodecahydronaphthalene gave no reaction even after prolonged heating to 80 °C. Presumably, the decreased Lewis basicity of the C-F bonds in these substrates precludes interaction with the Lewis acidic hydridoborane that initiates the reactions above.

To probe the mechanisms of these borane/C-F reactions, DFT calculations at the TPSS-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-TZVP + COSMO level[9a, 28] were performed. Reactions of dimeric borane $[(C_6F_5)_2BH]_2$ with Ad-F, Cy-F and Bn-F (benzyl fluoride) in CH_2Cl_2 solution were computed (Figure 2). In all cases, the initial dissociation of diborane into two monomers is the rate-limiting step and 7.0 kcal/mol endergonic over a barrier (via TS1) of 17.6 kcal/mol. For comparison, the initial dissociation of diborane $(9\text{-BBN})_2$ into two monomers 9-BBN is 17.6 kcal/mol endergonic over a higher barrier of 22.5 kcal/mol, consistent with its slower reactions with C-F bonds. The adduct (Ad-F)·$(C_6F_5)_2BH$·exhibits considerable ionic character with elongated B-F and F-C bonds (1.596 and 1.633 Å, respectively). Both hydride and C_6F_5 transfer from the borane to Ad occurs via contact-ion-pair-like transition structures TS2 and TS3 affording Ad-H and $(C_6F_5)_2BF$ or Ad-C_6F_5 and $(C_6F_5)BFH$, respectively. Consistent with experiment, the former hydride transfer is computed to be 1.5 kcal/mol kinetically more favourable. The transient borane $(C_6F_5)BFH$ either dimerizes to $[(C_6F_5)BFH]_2$ or disproportionates to minor amounts of $(C_6F_5)BF_2$ and $(C_6F_5)BH_2$ via a bimolecular H/F exchange process. While the separated ion pair $[Ad]^+[(C_6F_5)_2BHF]^-$ is also thermodynamically accessible (via TS4-h) from the adduct (Ad-F)·$(C_6F_5)_2BH$, this is inconsistent with experimental data. Hydride transfer to give Ad-H (via TS4)[29] is computed to be 15 kcal/mol higher barrier than for aryl transfer (see ESI), whereas Ad-C_6F_5 is experimentally observed in 23% yield.

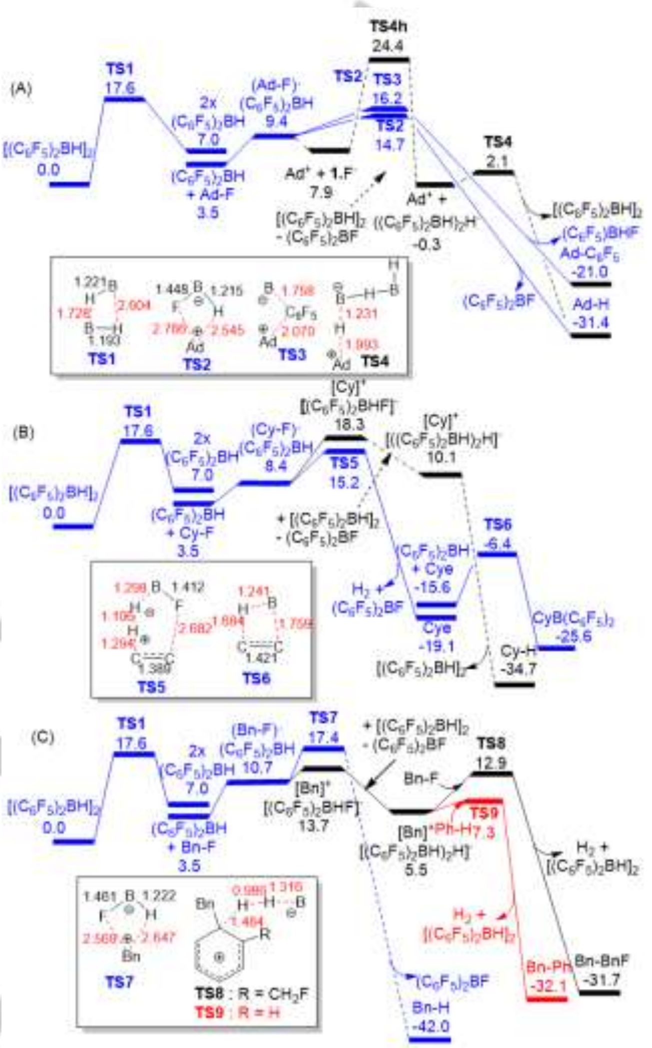


Figure 2. DFT-computed free energy paths (ΔG at 298 K for each step in kcal/mol, barrier in parentheses) for typical reactions of dimeric borane $[(C_6F_5)_2BH]_2$ with (A) Ad-F, (B) Cy-F and (C) Bn-F in CH_2Cl_2 solution, obtained at the TPSS-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-TZVP + COSMO level of theory. Cye = cyclohexene. In depicting the cores of the transition states, substituents on B and C are omitted for clarity. Selected bond lengths (in Å) are shown.

The adduct (Cy-F)·$(C_6F_5)_2BH$ is less ionic in nature with a longer B-F but a shorter F-C distances (1.784 and 1.515 Å, respectively). Hydride transfer from $(C_6F_5)_2BH$ to the β-hydrogen (proton) of Cy proceeds via the contact-ion-pair-like transition structures TS5 yielding H_2 gas and cyclohexene (Cye). Borane dimer dissociation is again rate-limiting. Side-reactions such as aryl and hydride transfer from borane $(C_6F_5)_2BH$ to the β-hydrogen (proton) were computed to be kinetically less competitive by 10.1 and 8.3 kcal/mol (see ESI). Similarly, a pathway involving a separated ion pair $[Cy]^+[(C_6F_5)_2BHF]^-$ is high-energy and thus not favoured. The subsequent addition of borane to Cye to form the main product $CyB(C_6F_5)_2$ is 10.0 kcal/mol exergonic over a rather low barrier (via TS6) of only 9.2 kcal/mol and is kinetically favoured. While a similar mechanism with a higher overall barrier of 23.8 kcal/mol is supported (see ESI) for the reaction of Pent-F, the observation of 1-pentene and pentane is consistent with competing hydride transfer to the β-hydrogen (proton) and the cationic α-carbon of pentyl group.

The adduct (Bn-F)·$(C_6F_5)_2BH$ is computed to have an ionic nature with elongated B-F and F-C bonds (1.632 and 1.568 Å, respectively). Hydride transfer to Bn occurs via the transition structure TS7 affording toluene and $(C_6F_5)_2BF$. However, direct dissociation of (Bn-F)·$(C_6F_5)_2BH$ to the ion pair $[Bn]^+[(C_6F_5)_2BHF]^-$ is kinetically favourable due to solvation of the $[Bn]^+$ cation. Trapping of the transient $[Bn]^+$ cation by benzene molecule is computed to be nearly barrierless via TS9, consistent with experiment.

In summary, we have uncovered that hydridoboranes can be used to reduce C(sp^3)-F bonds at ambient conditions without the use of catalysts or initiators. In particular, the electrophilic borane $HB(C_6F_5)_2$ was shown to be reactive with secondary and primary fluoroalkanes, affording initial olefinic products via dehydrofluorination, which in the presence of additional hydridoborane affords a net C-F borylation. This constitutes, to the best of our knowledge, the only example of catalyst-free C(sp^3)-F borylation involving a neutral hydridoborane reagent. While 9-BBN and $(C_6F_5)_2BH$ effect hydrodefluorination of tertiary C-F bonds, benzyl fluorides undergo Friedel-Crafts chemistry in the presence of arene solvents. Overall, this provides new routes to C-F borylation and room temperature Friedel-Crafts chemistry. We are continuing to develop strategies and applications using main group species to effect chemistry of C-F bonds.

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Keywords: hydridoboranes • Alkyl-fluorides • C-F reduction • borylation • Friedel-Crafts

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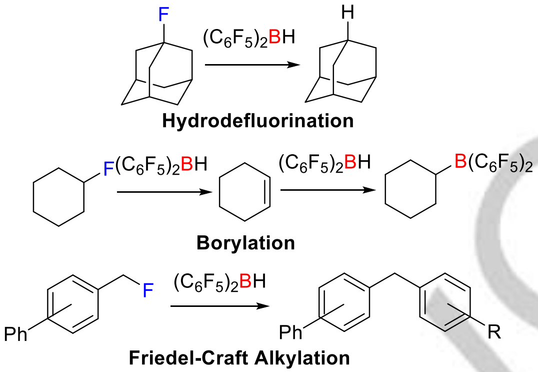
Entry for the Table of Contents

COMMUNICATION

Interactions of C-F bonds with hydridoboranes: Reduction, Borylation and Friedel-Crafts Alkylation: Hydridoboranes react with primary, secondary and tertiary C-F bonds under ambient conditions affording either hydrodefluorination, dehydrofluorination, C-F borylation or Friedel-Crafts chemistry alkylation.



Karlee Bamford, Saurabh Chitnis, Zheng-Wang Qu and Douglas W. Stephan**

Page No. – Page No.

Interactions of C-F bonds with hydridoboranes: Reduction, Borylation and Friedel-Crafts Alkylation