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Reversible, Metal-Free, Heterolytic Activation of H_2 at Room Temperature

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Hydrogen storage materials[1] derived from main group compounds and amino-boranes in particular have been the focus of numerous recent experimental[2−14] and theoretical studies.[15−21] Generally, such materials liberate H_2 either catalytically or under thermal duress. Unfortunately, none of these main group systems that evolve H_2 are easily regenerated. Nevertheless, the uptake of H_2 by main group systems has also been examined, albeit to a lesser extent. While spectroscopic studies have probed the interactions of main group compounds with H_2 in an argon matrix,[22] Power and co-workers were the first to report the uptake of H_2 by a digermyne to give a mixture of digermene, digermane, and primary germane products.[23] In our own efforts, we have described the concept of "frustrated Lewis pairs" (FLPs), in which combinations of Lewis acids and Lewis bases are sterically precluded from adduct formation and activate H_2.[24,25] In 2006, we described the first main group system capable of *reversible* H_2 activation. The zwitterion $[(2,4,6\text{-}C_6H_2Me_3)_2P(H)(C_6F_4)B(H)(C_6F_5)_2]$ was shown to liberate H_2 upon heating to 150 °C, while remarkably the resulting phosphine−borane $(2,4,6\text{-}C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ reacts with H_2 at room temperature to regenerate the starting phosphonium borate.[26] This finding illustrated that unquenched Lewis acidity and Lewis basicity can be exploited for the activation of small molecules. In a similar fashion, heterolytic cleavage of H_2 was achieved with sterically encumbered phosphine/borane combinations yielding the phosphonium borates $[R_3PH]$ $[HB(C_6F_5)_3]$ ($R = t$-Bu, $2,4,6\text{-}C_6H_2Me_3$).[27] We and others have applied the concept to activate H_2 with FLPs derived from (alkyl)(amino)carbenes,[28] phosphinoalkylboranes,[22] and $R_2PB(C_6F_5)_2$[29] as well as combinations of $B(C_6F_5)_3$ with sterically demanding amines,[30−32] imines,[30,33] or *N*-heterocyclic carbenes.[34] While the discovery of these metal-free systems that activate H_2 has focused attention on applications in catalytic hydrogenation,[30,32,33,35] the catalyst derived from 1,8-$(PPh_2)_2C_{10}H_6$ and $B(C_6F_5)_3$, recently reported by Erker et al., is the only other system[35] known to take up H_2 at 25 °C and release it under thermal duress (60 °C). Herein, we describe a simple phosphine/borane combination that reversibly activates and releases H_2 at room temperature.

The metal-free H_2 activation by combinations of sterically encumbered phosphines R_3P ($R = t$-Bu, $2,4,6\text{-}C_6H_2Me_3$) with $B(C_6F_5)_3$ is remarkable. Nonetheless the resulting salts do not liberate H_2 under thermal duress to 150 °C. This inability was attributed to the Lewis basicity of the R_3P and the Lewis acidity of the $B(C_6F_5)_3$ fragments, respectively. Thus we have explored systematic modifications of the Lewis-acidity and basicity of FLP constituents for the design of systems capable of reversible H_2 binding. Reducing the Lewis acidity of the borane has been shown to significantly diminish the ability to activate H_2,[27] whereas the electrophilicity of $B(C_6F_5)_3$ generates a tightly bound hydride in the resulting borate. In addition, nucleophilic aromatic substitution at the *para*-position of a C_6F_5 ring on $B(C_6F_5)_3$ was observed when less sterically demanding phosphines were employed, yielding zwitterions of the form $[R_3P(C_6F_4)B(F)(C_6F_5)_2]$.[36]

To address both concerns, we targeted the hitherto unknown borane $B(p\text{-}C_6F_4H)_3$ **1**. Its synthesis was accomplished via a Knochel-type in situ generation of the Grignard reagent (p-$C_6F_4H)MgBr$ in Et_2O from the commercially available bromofluoroarene $p\text{-}C_6F_4HBr$ utilizing *i*-PrMgCl.[37] Subsequent reaction with $(Et_2O)BF_3$ gave, upon workup and isolation, the etherate $(Et_2O)B(p\text{-}C_6F_4H)_3$ **2** as a colorless solid in 68% yield. Treatment of this initial product with Me_2SiHCl and removal of all volatiles afforded **1** as a colorless solid. It was further purified either by sublimation in vacuo at 120 °C to give fluffy needles or by precipitation from saturated hydrocarbon solutions at −35 °C. Employing the Gutmann−Beckett[38−41] and Childs[42] methods, compound **1** was shown to exhibit about 5% less Lewis acidity in comparison to the fully fluorinated borane, $B(C_6F_5)_3$.[36,43]

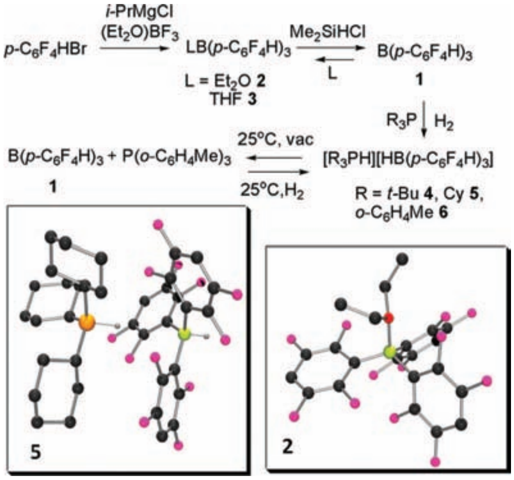

Figure 1. Synthesis of $B(p\text{-}C_6F_4H)_3$ **1** and the reversible activation of H_2 at ambient temperature.

The ^1H NMR spectrum of **1** shows a diagnostic triplet of triplets at 6.74 ppm as a result of the two types of couplings ($^3J_{HF}$ and $^4J_{HF}$) exhibited by the hydrogen atoms in the para positions. The broad ^{11}B resonance at 59 ppm and the ^{13}C and ^{19}F NMR spectra are all as anticipated. Though efforts to crystallize **1** were unsuccessful, addition of Et_2O or THF to hydrocarbon solutions of **1** readily afforded the adducts **2** and $(THF)B(p\text{-}C_6F_4H)_3$ **3**, respectively. An X-ray structure was obtained for the ether adduct **2**, establishing the formulation unambiguously (Figure 1).[44]

The ability of the borane **1** to participate in an FLP to effect H_2 activation was confirmed. Dissolving combinations of **1** and bulky phosphines R_3P resulted in no apparent reactions as evidenced by ^1H, ^{31}P, ^{19}F, and ^{11}B NMR spectroscopy. Subsequent addition of H_2 prompted its spontaneous heterolytic cleavage reaction to afford the salts $[R_3PH][HB(p\text{-}C_6F_4H)_3]$ ($R = t$-Bu **4**, Cy **5**, $o\text{-}C_6H_4Me$ **6**), each isolated in near quantitative yield. The spectroscopic data are fully consistent with these formulations. As an example, compound

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4 gives rise to doublets at 5.21 and 56.6 ppm in ^{1}H and ^{31}P NMR, respectively, both with a $^1J_{HP}$ coupling constant of 445 Hz, consistent with the formation of a phosphonium cation. Similarly, a ^{1}H NMR quartet signal at 4.15 ppm and an ^{11}B NMR doublet signal at −23.7 ppm, both with a $^1J_{HB}$ coupling of 90 Hz, support the presence of a hydridoborate anion. Similar spectral parameters were seen for **5** and **6**.

The salt **5** is of particular interest, as the corresponding reaction of Cy_3P and $B(C_6F_5)_3$ rapidly gives the zwitterion $[Cy_3P(C_6F_4)B(F)(C_6F_5)_2]$.[36] Similarly, Cy_3P and $[Ph_3C][B(C_6F_5)_4]$ react via nucleophilic para attack followed by proton migration to give $[Cy_3P(C_6H_4)CHPh_2][B(C_6F_5)_4]$.[45] The formation of **5**, confirmed by X-ray crystallography,[44] underlines the fact that replacement of F by H at the *para* positions of the arene rings precludes nucleophilic aromatic substitution on the borane **2**, while maintaining sufficiently high Lewis-acidity to effect H_2 activation in combination with a sterically encumbered phosphine base.

The reversibility of H_2 activation was examined with various experiments. Heating solutions of **4** and **5** to 80 °C under vacuum resulted in no reaction, a situation similar to that reported for the salts $[R_3PH][HB(C_6F_5)_3]$ (R = *t*-Bu, 2,4,6-$C_6H_2Me_3$).[27] By contrast, placing a solution of **6** under static vacuum at 25 °C that was periodically renewed for several days resulted in the slow liberation of H_2. The concurrent generation of free phosphine and borane was evidenced by NMR spectroscopy. After 9 days, the conversion was 85% complete. In contrast $[(o\text{-}C_6H_4Me)_3PH]$ $[HB(C_6F_5)_3]$ **7**, showed no signs of H_2 liberation under the same conditions. The room temperature loss of H_2 by compound **6** was further supported by storing a solution of it under an atmosphere of D_2. This resulted in the slow incorporation of deuterium generating the deuterium-enriched salt $[(o\text{-}C_6H_4Me)_3P(H/D)]$ $[(H/D)B(p\text{-}C_6F_4H)_3]$ as evidenced by the observation of additional 1:1:1 triplet in the ^{31}P NMR spectrum at −12.5 ppm ($^1J_{PD}$ = 70 Hz) and a broad signal in the ^{11}B NMR spectrum at −24.2 ppm. Liberation of H_2 was accelerated when a solution of **6** was heated to 80 °C under vacuum, yielding 85% of free phosphine and borane overnight. Under these latter conditions, the loss of H_2 was also observed in the solid state, as storage of solid **6** at 80 °C under static vacuum overnight gave 60% yield of the FLP as evidenced by NMR spectroscopy.

In conclusion, the judicious combination of $(o\text{-}C_6H_4Me)_3P$ and the borane **1** strikes the right balance of acidity and hydridicity to allow reversible H_2 binding at 25 °C. Such systems may prove useful in H_2 transport and delivery applications where high per mass capacity is not an issue. However, these findings further suggest it may be possible to apply the reactivity of FLPs to develop new approaches to H_2 storage. Efforts to this end are underway and will be reported in due course.

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Supporting Information Available: Experimental procedures and X-ray crystallographic details of **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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