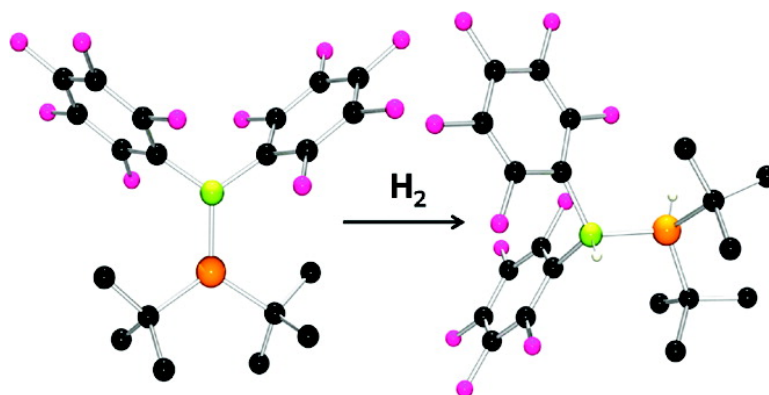


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Activation of H₂ by Phosphinoboranes R₂PB(C₆F₅)₂

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The potential of hydrogen storage materials¹ has focused much recent experimental^{2–14} and theoretical studies^{15–20} on main group compounds and amino-boranes in particular. While the liberation of H₂ has been a focus, a critical yet less explored issue involves the uptake of H₂ by main group species. Early studies described the interactions of H₂ with main group compounds in an argon matrix;²¹ however, it was not until the work of Power and co-workers²² that a main group species was shown definitively to react with H₂. In that work, germynes were hydrogenated to give a mixture of digermene, digermane, and primary germane products. In 2006, we described the room temperature addition of H₂ to (C₆H₂Me₃)₂P(C₆F₄)B(C₆F₅)₂ to give the phosphonium borate salt (C₆H₂Me₃)₂PH(C₆F₄)BH(C₆F₅)₂.²³ In an elegant and related work, Bertrand and co-workers²⁴ subsequently showed that sterically demanding alkyl-amino-carbenes activate H₂ to convert the carbene carbon to a methylene fragment. We further showed that simple combinations of Lewis acids and bases such as *t*Bu₃P/B(C₆F₅)₃ are sterically precluded from forming a dative bond and effect heterolytic cleavage of H₂ to give [*t*Bu₃PH][HB(C₆F₅)₃].²⁵ Lewis acid/base combinations, termed “frustrated Lewis pairs”, capable of H₂ activation have been extended to include alkyl-linked phosphine-boranes,²¹ as well as mixtures of B(C₆F₅)₃ with sterically crowded imines,^{26,27} amines,^{26,27} and N-heterocyclic carbenes.²⁸ In considering the application of this concept to systems more closely related to amino-boranes, we note the recent computational study by Manners and co-workers²⁹ that suggested the combination of electron-donating and electron-withdrawing groups on N and B, respectively, would afford amido-boranes capable of reaction with H₂. Herein, we describe related phosphinoboranes with such electronic features and demonstrate that the combination of bulky electron-rich phosphides and electron-deficient B(C₆F₅)₂ fragments produces phosphinoboranes that undergo facile addition of H₂ to give the phosphine-borane adducts (R₂PH)(HBR′₂). This finding, in combination with DFT calculations, sheds light on the uptake of H₂ across a group 13–group 15 bond, a critical requirement for the development of a recyclable H₂ storage device based on amine-borane adducts.

Secondary lithium phosphides (R₂PLi R = Et, Ph, Cy, *t*Bu) were treated with (C₆F₅)₂BCl³⁰ in toluene at –35 °C and allowed to stir overnight. Subsequent workup afforded the colorless pentane insoluble, crystalline materials **1–4**, respectively, in isolated yields ranging from 61 to 83%. In all cases the ¹H and ¹³C{¹H} NMR data were consistent with the presence of the R₂P fragment in the product while the ¹⁹F NMR spectra revealed resonances attributable to the C₆F₅ rings on B. In the case of **1** and **2**, the ¹¹B NMR spectra showed triplet resonances at δ –12.9 and –2.2 with B–P coupling constants of 72 and 66 Hz and broad ³¹P NMR signals at δ –23.4 and –0.8, respectively. These data support the formulation of **1** and **2** as [(μ-R₂P)B(C₆F₅)₂]₂ dimers. In the case of **1** this was

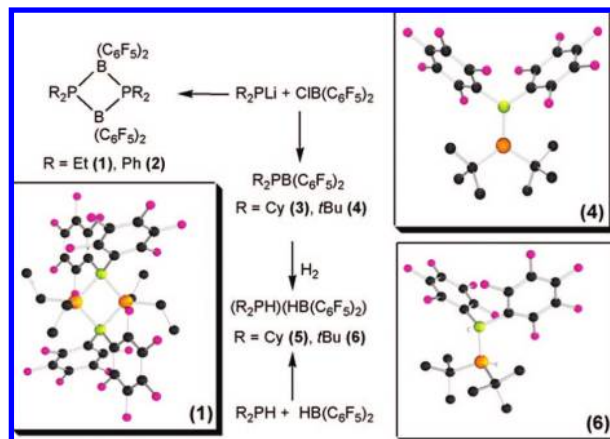


Figure 1. Synthesis and reactivity of phosphinoboranes. POV-ray drawings of **1**, **4**, and **6**. C: black, F: pink, P: orange, B: light green, H: white. All hydrogen atoms except BH and PH in **6** were omitted for clarity.

unambiguously confirmed via a crystallographic study. The products **3** and **4** exhibited simple doublet resonances at δ 39.5 and 41.8, respectively, in the ¹¹B NMR spectra with P–B coupling constants of 142 and 150 Hz, respectively. Species **3** and **4** were formulated as monomeric phosphinoboranes R₂PB(C₆F₅)₂. This was confirmed by an X-ray crystallographic study of **4** (Figure 1). The geometries about B and P are pseudotrigonal planar as the sum of the angles about B and P are 360.0° and 359.07°, respectively. The B–P distance in **4** is 1.786(4) Å, which is markedly shorter than that observed for **1** (B–P_{avg} 2.057(3) Å) and a number of related B–P species.^{31,32}

Reactions of the phosphinoboranes **1–4** with H₂ were examined. Solutions of each phosphinoborane were pressurized under 4 atm of H₂ and allowed to stand at 25 °C. Monitoring of the reactions by NMR spectroscopy over a period of 4 weeks revealed no reaction of the dimeric phosphinoboranes **1** and **2**. In contrast, the species **3** and **4** underwent slow addition of H₂ to afford the phosphineborane adducts (R₂PH)(BH(C₆F₅)₂) (R = Cy **5**, *t*Bu **6**). In the case of **3**, the formation of **5** was complete at 25 °C in 2 weeks, whereas the corresponding reaction of **4** afforded **6** in 80% yield in 4 weeks. In contrast, at 60 °C the reactions of **3** and **4** with H₂ resulted in the quantitative formation of **5** and **6**, respectively, in 48 h. Identification of **5** and **6** was confirmed by independent syntheses, as treatment of the corresponding secondary phosphines with the borane (C₆F₅)₂BH³⁰ yielded adducts **5** and **6** in 77 and 65% isolated yields, respectively. NMR data for **5** and **6** were characteristic of these species as doublets at δ 4.78 and 4.84 in the ¹H NMR spectra exhibiting P–H coupling constants of 381 and 375 Hz, respectively. In addition, resonances attributable to the BH fragment were observed at δ 3.33 and 3.48 for **5** and **6**, respectively. The corresponding ³¹P NMR resonances for **5** and **6** were observed at δ 7.1 and 32.0, respectively, while the ¹¹B NMR signals occurred

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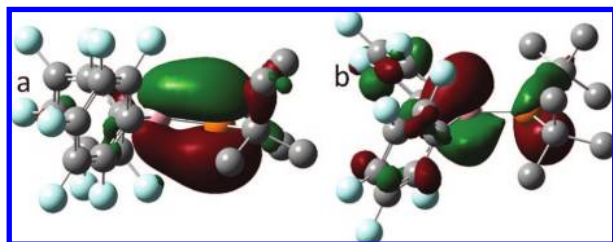


Figure 2. Gaussview drawing of the (a) HOMO and (b) LUMO of **4**. C: gray, F: blue, P: orange, B: pink. Hydrogen atoms were omitted for clarity.

at δ -28.1 and -30.0 , respectively, with P–B coupling constants of 68 and 48 Hz. Identification of **6** is further confirmed via X-ray crystallography (Figure 1). The geometry about both B and P was pseudotetrahedral with hydrogen atoms adopting an *anti* orientation. The B–P distance in this adduct was found to be $1.966(9)$ Å, dramatically longer than that seen in **4**.

The nature of BP bonding in **4** and the mechanism of its reaction with H_2 were examined computationally. Optimization of **4** at the MPW1K/BSO level provides a structure in good agreement with that obtained crystallographically (BP = 1.808 Å, angles C–B–C = 113.3° , C–B–P = 123.1° , C–P–B = 120.2° , C–P–C = 115.3°). The natural bond order (NBO) model based on the optimized wave function indicates the presence of a BP π bonding orbital as the HOMO (Figure 2). The π bond is significantly polarized, in that it is composed of 26% natural boron orbitals and 74% natural phosphorus orbitals.³³

Relaxed scans (ONIOM2 MPW1K) of the potential energy surface for H_2 addition to **4** (carried out scanning its microscopic reverse as H_2 loss from **6**) revealed that H_2 initially attacks the Lewis acidic boron, using the H–H bond as a Lewis base. Thereafter, the coordinated H_2 rotates so that its bond lies parallel to the BP bond, whereupon the H atom closest to phosphorus traverses the BP bond, splitting the H–H bond and forming the new P–H bond. Coordination of H_2 to boron represents the barrier for the process, estimated to be ca. 22 kcal mol⁻¹ by this approach. Subsequent steps as outlined are essentially barrierless. The exothermicity of the process (-43 kcal mol⁻¹) combined with the barrier energy indicates that it is irreversible. Indeed, this view is consistent with the observation that heating of **5** or **6** to 100 °C for 24 h resulted in no observed reaction. This result stands in contrast to the thermolysis of the phosphine-borane adducts of the form $R_2PH(BH_3)$ which have been shown to thermally or catalytically eliminate H_2 to form cyclic and polymeric phosphinoboranes,^{34–36} suggesting that the reactivity of the present systems is suppressed by the presence of the electron-withdrawing substituents on B.

The reactivity of **3–6** is consistent with the theoretical predictions made for amido-boranes²⁹ albeit with the replacement of N with P. The present chemistry experimentally demonstrates that incorporation of large electron-donating groups on the donor, group 15 atom and electron-withdrawing groups on the acceptor B atom affords monomeric phosphinoboranes capable of reaction with H_2 , while such substitution also enthalpically disfavors dehydrogenation. Mismatch of the energies of the P lone pair and the vacant B p-orbital gives rise to the strong polarity of the P–B π -bond and presumably prompts reactivity with H_2 . Thus, this work provides

insight on molecular features required for H_2 uptake, a critical issue for the design of a fully recyclable H_2 storage material. We continue to explore group 13/15 systems seeking to apply the concept of “frustrated Lewis pairs”³⁷ to uncover and apply new systems capable of activation of H_2 as well as other small molecules to material design and catalysis.

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Supporting Information Available: Experimental and computational details. For crystallographic data, see: CCDC 691485–691487. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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