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Reversible, Metal-Free Hydrogen Activation

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Although reversible covalent activation of molecular hydrogen (H_2) is a common reaction at transition metal centers, it has proven elusive in compounds of the lighter elements. We report that the compound $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ (Me, methyl), which we derived through an unusual reaction involving dimesitylphosphine substitution at a para carbon of tris(pentafluorophenyl) borane, cleanly loses H_2 at temperatures above $100^\circ C$. Preliminary kinetic studies reveal this process to be first order. Remarkably, the dehydrogenated product $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ is stable and reacts with 1 atmosphere of H_2 at $25^\circ C$ to reform the starting complex. Deuteration studies were also carried out to probe the mechanism.

The generation and use of H_2 are important processes to fundamental chemical transformations (1–7) and biological functions (8). The overwhelming majority of systems known to either liberate or react with H_2 involve reaction at a transition metal center. Hydrogenase enzymes, as well as a plethora of synthetic stoichiometric and catalytic reagents for hydrogenation reactions, are based on the processes of oxidative addition and reductive elimination of H_2 at a metal center. Metal-free systems that either react with or liberate H_2 are rare. A unique metal-free hydrogenase from methanogenic archaea has been shown to catalyze reactions with H_2 (9–11), and theoretical studies suggest the role of a folate-like cofactor in the reversible activation or liberation of H_2 (12, 13). Several metal-free systems have been shown to activate H_2 . For example, main group element- H_2 reactions (14) in low-temperature matrices have been reported (15–17), and computational studies have probed the occurrence of H_2 bonds in main-group compounds (18, 19). More recently, Power and co-workers (20) reported that the addition of H_2 to Ge_2 -alkyne analogs affords a mixture of Ge_2 and primary germane products. Metal-free systems that liberate H_2 are of interest for their potential in H_2 storage applications. Although much effort has focused on hydride salts (21–23), a recent report by Thorn and co-workers describes an organic “hydride” system that reacts with protic compounds to

eliminate H_2 , although the assistance of a metal-based catalyst is required (24). Despite these advances, no metal-free system is yet reported to effect both the clean liberation and addition of H_2 .

Here we report a phosphonium-borate species that undergoes thermally induced loss of H_2 to generate the corresponding phosphine-borane. We discovered this reaction sequence in the course of our studies on phosphine-

borane interactions. The well-known Lewis acidic polymerization cocatalyst $B(C_6F_5)_3$ behaves as a traditional Lewis acid with donor molecules to form simple Lewis acid-base adducts (25, 26). However, we have discovered that the sterically demanding secondary phosphine $(C_6H_2Me_3)_2PH$ reacts with $B(C_6F_5)_3$ to effect para-nucleophilic aromatic substitution, affording the zwitterionic phosphonium-borate $(C_6H_2Me_3)_2PH(C_6F_4)BF(C_6F_5)_2$ **1** (27) (Fig. 1).

The white, air- and moisture-stable solid **1** was isolated in 78% yield and exhibited a single phosphonium resonance in the $^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectrum at -37.7 ppm as well as resonances in the ^{19}F NMR spectrum consistent with the presence of a BF bond and C_6F_4 and C_6F_5 rings. The corresponding ^{11}B NMR resonance revealed B-F coupling, and the 1H NMR spectrum showed a doublet at 8.52 ppm from the PH fragment. Upon cooling to $-15^\circ C$, the ^{19}F NMR resonances of the C_6F_4 bridge at -134 and -129 ppm split into doublets, consistent with inhibited rotation about the P- C_6F_4 bond. The thermodynamic barrier to this rotation was determined by variable-temperature NMR spectroscopy to be

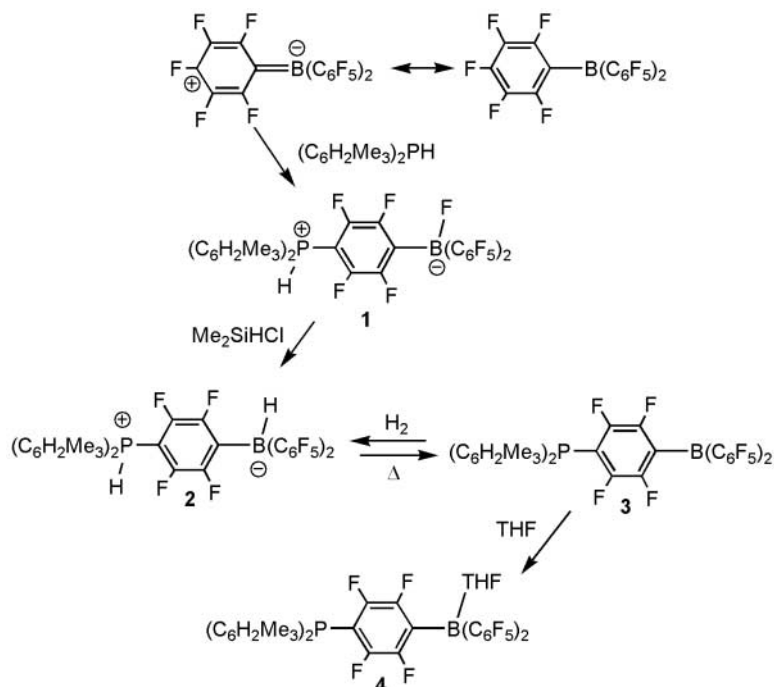


Fig. 1. Syntheses of compounds **1** to **4**.

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$\Delta G = 51.1 \pm 0.5 \text{ kJ mol}^{-1}$. The formation of **1** implies that $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PH}$ is too large to coordinate to the B of $\text{B}(\text{C}_6\text{F}_5)_3$, prompting the observed aromatic substitution. In a similar fashion, Erker and co-workers reported the thermally induced rearrangement of an yldeborane adduct $(\text{Ph}_3\text{PCHPh})\text{B}(\text{C}_6\text{F}_5)_3$ (Ph, phenyl) to the para-substituted phosphonium-borate $(\text{Ph}_3\text{PCHPh})(\text{C}_6\text{F}_4)\text{BF}(\text{C}_6\text{F}_5)_2$ (**28**).

Compound **1** rapidly reacted with Me_2SiHCl to give $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PH}(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ **2** via H-for-F exchange. The white solid **2** exhibited a ^{11}B NMR signal at -25.2 ppm indicative of a four-coordinate boron hydride, whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at -34.3 ppm was largely unchanged from that of **1**. The ^1H NMR spectrum showed doublet and quartet resonances at 8.49 ppm and 3.65 ppm , respectively, arising from the P-H and B-H fragments. A crystallographic study of **2** confirmed the proposed connectivity of $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PH}(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ (**27**, **29**) (Fig. 2A). Thus, the air- and moisture-stable phosphonium-borate **2** can be prepared in a unique and facile two-step synthesis from readily available precursors (**27**).

In toluene solution, compound **2** underwent stoichiometric loss of H_2 in a facile manner upon heating above 100°C . The loss of H_2 was confirmed by the subsequent quantitative formation of the red-orange phosphinoborane species $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{P}(\text{C}_6\text{F}_4)\text{B}(\text{C}_6\text{F}_5)_2$ **3** (**27**) (Fig. 1). It is noteworthy that phosphine-borane adducts of the form $\text{R}_2\text{PH}(\text{BH}_3)$ are also known to thermally or catalytically eliminate H_2 to give cyclic and polymeric phosphinoboranes (**30**, **31**). Monitoring the thermal decomposition of **2** by ^{19}F NMR spectroscopy showed a shift in the resonances attributed to the para-F of the C_6F_5 rings from -164 to -143 ppm , consistent with a change from four- to three-coordinate boron (**32–34**). Loss of the PH and BH resonances in the ^1H NMR and an upfield shift of 4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum confirmed the loss of H_2 from **2** and formation of **3**. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** revealed a barrier to P– C_6F_4 bond rotation of 42.7 kJ mol^{-1} , which is lower than that seen in **1**, consistent with the absence of $\text{H}\cdots\text{ortho-F}$ interactions in **3**. Weak π -donation from P and electron acceptance by B has been proposed for the related acetylene-based phosphinoborane $\text{Ph}_2\text{PCCB}(\text{C}_6\text{H}_2\text{Me}_3)_2$ (**35**, **36**); thus, on the basis of the intense red-orange color of **3** in solution (wavelength for maximum absorption $\lambda\text{-max}$, 455 nm ; molar absorption coefficient $\epsilon = 487 \text{ liters cm}^{-1} \text{ mol}^{-1}$) (Fig. 2C), it is tempting to attribute this color to an internal charge transfer.

The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift for **3** showed minimal change with temperature, an observation consistent with the persistence of a pyramidal geometry at P. Nonetheless, polarization of charge in this donor-acceptor molecule may account for the observed color. Coordination of Lewis bases to B rendered

the species colorless. As an example, recrystallization of **3** in the donor solvent tetrahydrofuran (THF) afforded colorless single crystals of the THF adduct **4**. This species exhibited NMR spectral data similar to **3** with additional resonances attributed to coordinated THF. A crystallographic study of **4** confirmed the formulation as $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{P}(\text{C}_6\text{F}_4)\text{B}(\text{THF})(\text{C}_6\text{F}_5)_2$ (**27**, **29**) (Fig. 2B); the geometry about B was pseudo-tetrahedral with THF coordination.

Remarkably, the isolated compound **3** reacted with H_2 in solution at 25°C . This reaction proceeded smoothly with rapid loss of the orange color to give a colorless solution of **2** (Fig. 2C). NMR data showed that the conversion to **2** was quantitative in less than 5 min. Thus, the thermally induced loss of H_2 from **2** was readily reversed. This reaction of **3** with H_2 was subsequently shown to be rapid even at -25°C . In a similar fashion, **3** reacted with D_2 to give the corre-

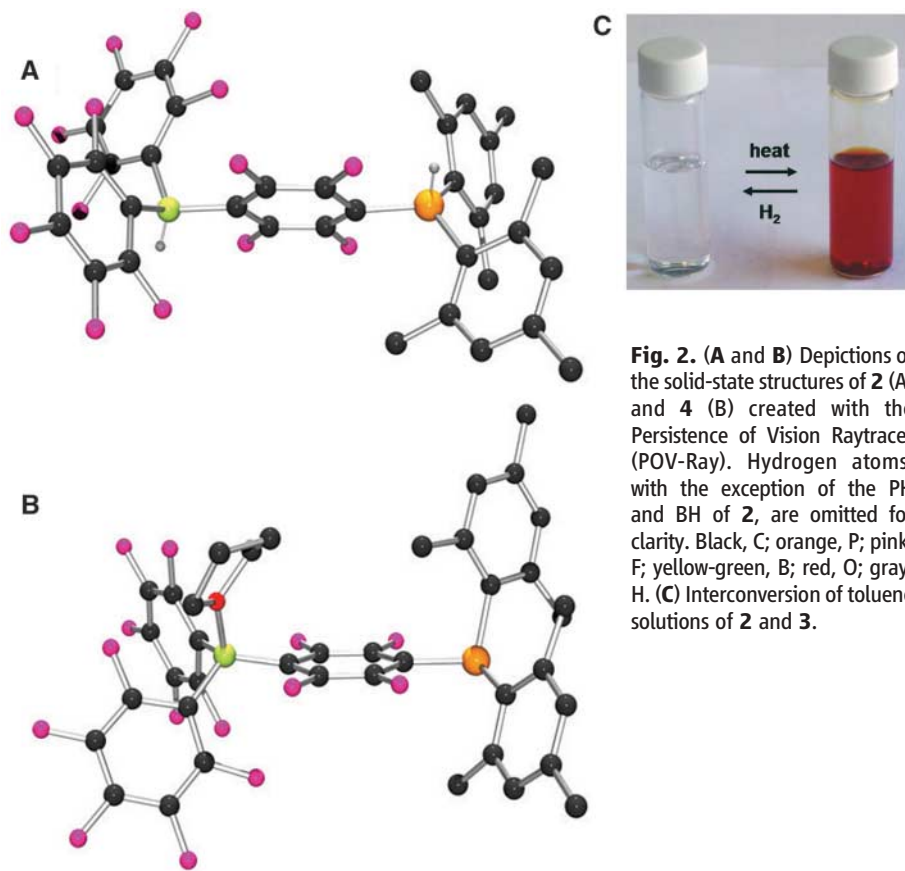


Fig. 2. (A and B) Depictions of the solid-state structures of **2** (A) and **4** (B) created with the Persistence of Vision Raytracer (POV-Ray). Hydrogen atoms, with the exception of the PH and BH of **2**, are omitted for clarity. Black, C; orange, P; pink, F; yellow-green, B; red, O; gray, H. (C) Interconversion of toluene solutions of **2** and **3**.

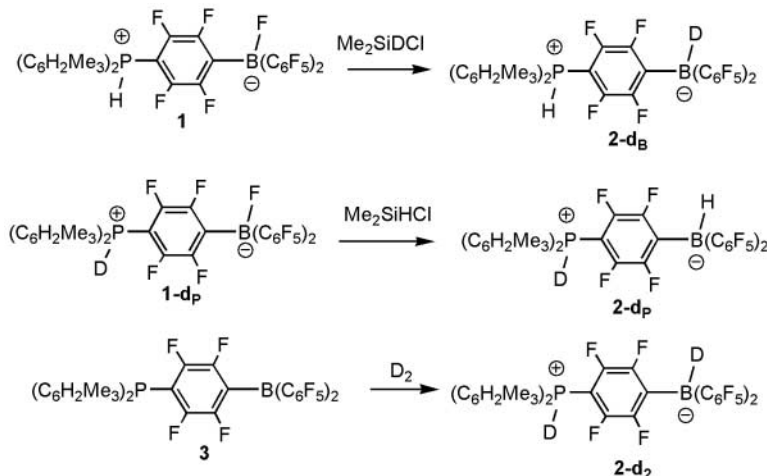


Fig. 3. Syntheses of the isotopomers of **2**.

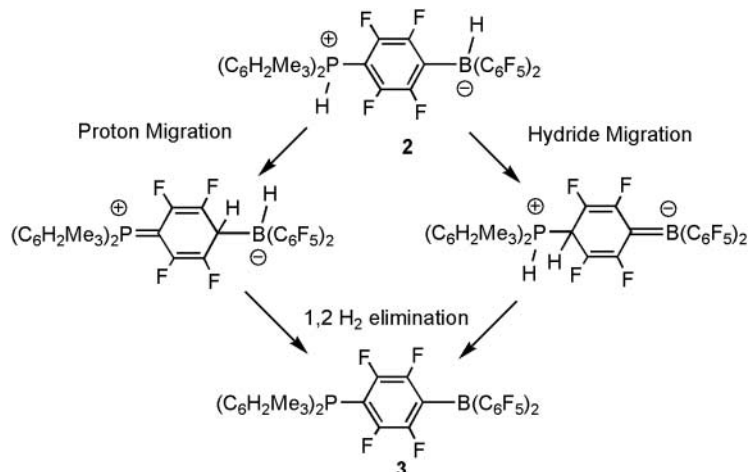


Fig. 4. Possible mechanisms for the formation of **3**.

sponding species $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PD}(\text{C}_6\text{F}_4)\text{BD}(\text{C}_6\text{F}_5)_2$ **2-d₂**. The site-specific labeled compound $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PH}(\text{C}_6\text{F}_4)\text{BD}(\text{C}_6\text{F}_5)_2$ **2-d_B** was prepared via reaction of **2** with Me_2SiDCl . Alternatively, the species $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PD}(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$ **2-d_P** was prepared following the procedure for **2** but using $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PD}$ to prepare **1-d_P**. These monodeuterated products (Fig. 3) showed no evidence of H-D exchange at 25°C; however, heating solutions of **2-d_B** or **2-d_P** to temperatures above 100°C in a sealed NMR tube, followed by cooling to 25°C, resulted in a statistical mixture of **2**, **2-d₂**, **2-d_P**, and **2-d_B**. This scrambling of H and D labels suggests the possibility of a high-temperature exchange process. To probe this finding further, we performed a conversion of a 1:1 mixture of **2** and **2-d₂** to **3**. The observation of HD in the statistical product mixture of H₂, D₂, and HD suggests a bimolecular high-temperature exchange process involving the intermolecular approach of BH and PH fragments in a transition state.

To gain further insight into this system, we acquired preliminary kinetic data. Initial rate data were obtained using $^3\text{P}\{^1\text{H}\}$ NMR spectroscopy to monitor the formation of **3** from the loss of H₂ by **2** in bromobenzene over the temperature range 100° to 150°C. Initially, spin-lattice relaxation time (T_1) measurements were performed to ensure that the relaxation delays were adequate to permit the correlation of integrals and concentrations. Over a concentration range of **2** from 0.02 M to 0.12 M, the consumption of **2** and generation of **3** were monitored over the first hour of reaction (27). These initial rate data showed that decay of the concentration of **2** followed first-order decay kinetics (figs. S1 and S2) with a rate constant of $3.5 \pm 0.6 \times 10^{-4} \text{ s}^{-1}$ at 140°C. Eyring plots (fig. S3) over the temperature range 100° to 150°C provided the enthalpy of activation $\Delta H^\ddagger = 90 \pm 1 \text{ kJ mol}^{-1}$ and entropy of activation $\Delta S^\ddagger = -96 \pm$

$1 \text{ J mol}^{-1} \text{ K}^{-1}$. The entropy value and the first-order kinetics are consistent with an intramolecular process, and the enthalpy value suggests substantial bond breakage in the transition state. Intramolecular H₂ elimination requires proton and hydride on adjacent atoms. This could be achieved by proton migration from P to the C adjacent to B, or alternatively by hydride migration from B to the C adjacent to P (Fig. 4). The present data do not allow us to explicitly distinguish between these possibilities. We speculate, on the basis of considerations of the microscopically reverse reaction where the uptake of H₂ by **3** is intuitively thought to be initiated by the interaction of H₂ with B, that proton migration is more likely. This view is supported by the fact that **4** did not react with H₂.

This reaction system demonstrates that reversible small-molecule activation is achievable in the absence of a transition metal. This finding foreshadows new vistas in metal-free reactions and catalysis. Similarly, although the present system reversibly binds less than 0.25 weight % H₂, which is much less than the targets of 6 to 9%, it does suggest that new strategies for chemical hydrogen storage may involve Lewis acid–Lewis base cooperative reactivity.

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Supporting Online Material

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Materials and Methods
Figs. S1 to S3
Tables S1 and S2
References

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