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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°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°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°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

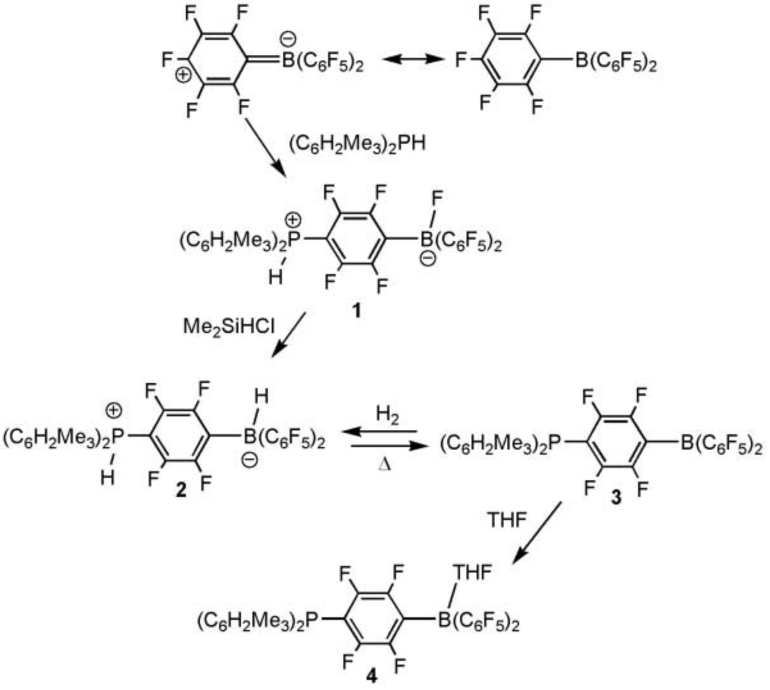

Fig. 1. Syntheses of compounds **1** to **4**.

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ΔG = 51.1 ± 0.5 kJ mol^{-1}. The formation of **1** implies that $(C_6H_2Me_3)_2PH$ is too large to coordinate to the B of $B(C_6F_5)_3$, prompting the observed aromatic substitution. In a similar fashion, Erker and co-workers reported the thermally induced rearrangement of an ylide-borane adduct $(Ph_3PCHPh)B(C_6F_5)_3$ (Ph, phenyl) to the para-substituted phosphonium-borate $(Ph_3PCHPh)(C_6F_4)BF(C_6F_5)_2$ (*28*).

Compound **1** rapidly reacted with Me_2SiHCl to give $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ **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 $^{31}P\{^1H\}$ 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 $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ (*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 $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ **3** (*27*) (Fig. 1). It is noteworthy that phosphine-borane adducts of the form $R_2PH(BH_3)$ 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 $^{31}P\{^1H\}$ NMR spectrum confirmed the loss of H_2 from **2** and formation of **3**. Variable-temperature $^{31}P\{^1H\}$ 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 H···ortho-F interactions in **3**. Weak π-donation from P and electron acceptance by B has been proposed for the related acetylene-based phosphinoborane $Ph_2PCCB(C_6H_2Me_3)_2$ (*35*, *36*); thus, on the basis of the intense red-orange color of **3** in solution (wavelength for maximum absorption λ-max, 455 nm; molar absorption coefficient ε = 487 liters cm^{-1} mol^{-1}) (Fig. 2C), it is tempting to attribute this color to an internal charge transfer.

The $^{31}P\{^1H\}$ 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 $(C_6H_2Me_3)_2P(C_6F_4)B(THF)(C_6F_5)_2$ (*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-

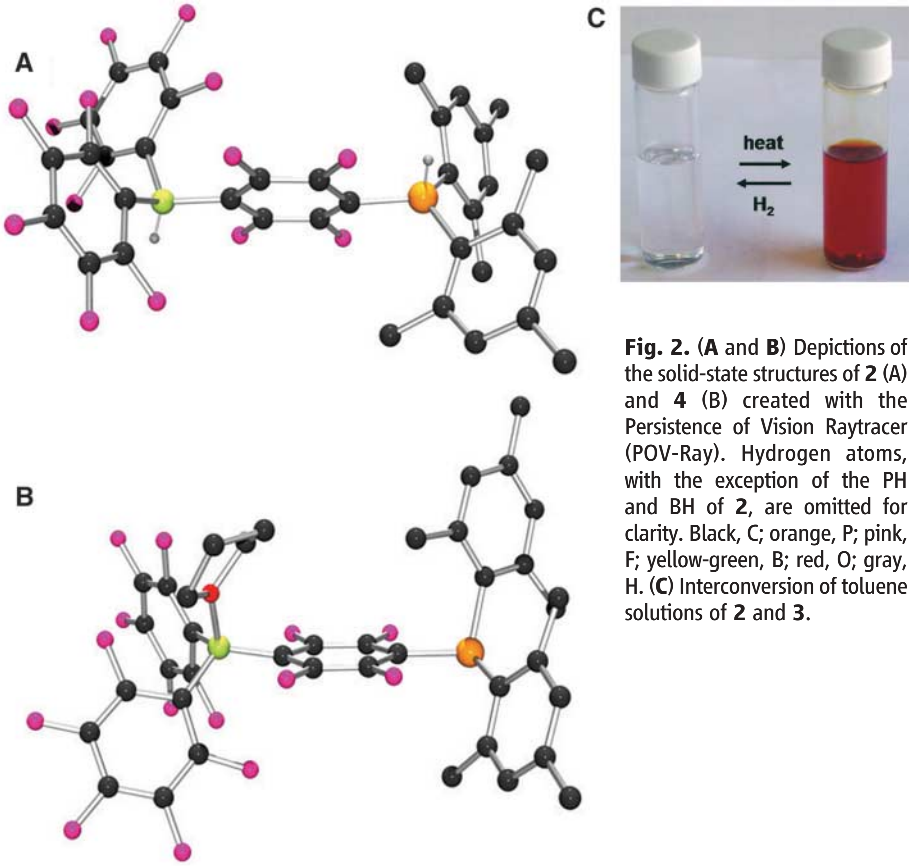

Fig. 2. (**A** and **B**) Depictions of the solid-state structures of **2** (A) and **4** (B) created with the Persistence of Vision Raytracer (POV-Ray). Hydrogen atoms, with the exception of the PH and BH of **2**, are omitted for clarity. Black, C; orange, P; pink, F; yellow-green, B; red, O; gray,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

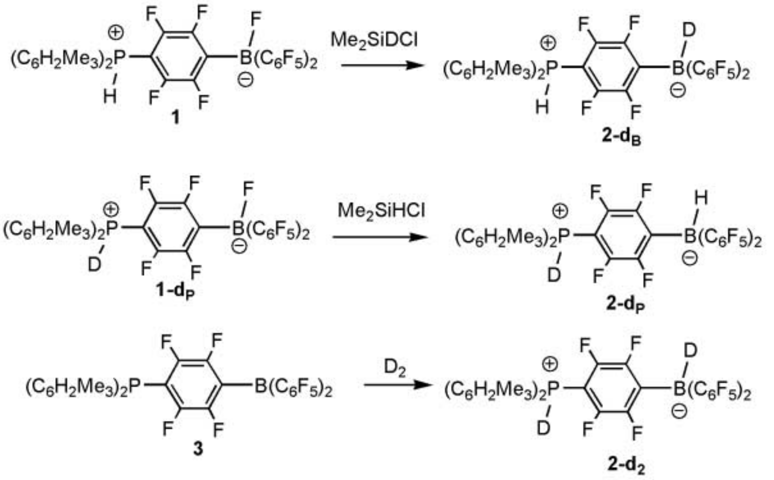

Fig. 3. Syntheses of the isotopomers of **2**.

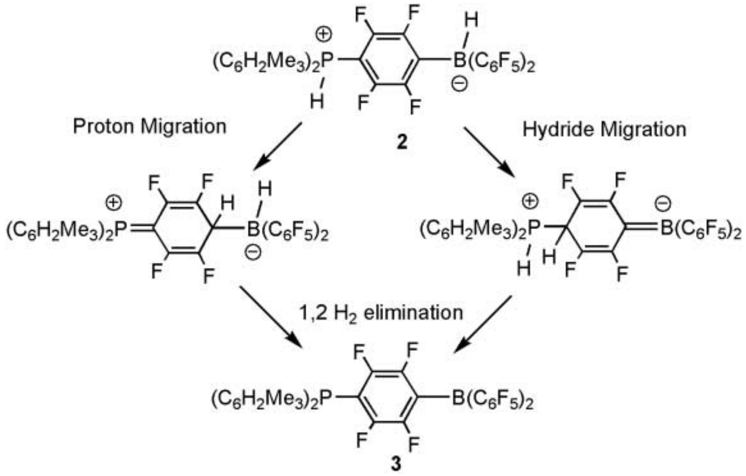

Fig. 4. Possible mechanisms for the formation of **3**.

sponding species $(C_6H_2Me_3)_2PD(C_6F_4)BD(C_6F_5)_2$ $\mathbf{2\text{-}d_2}$. The site-specific labeled compound $(C_6H_2Me_3)_2PH(C_6F_4)BD(C_6F_5)_2$ $\mathbf{2\text{-}d_B}$ was prepared via reaction of **2** with Me_2SiDCl. Alternatively, the species $(C_6H_2Me_3)_2PD(C_6F_4)BH(C_6F_5)_2$ $\mathbf{2\text{-}d_P}$ was prepared following the procedure for **2** but using $(C_6H_2Me_3)_2PD$ to prepare $\mathbf{1\text{-}d_P}$. These monodeuterated products (Fig. 3) showed no evidence of H-D exchange at 25°C; however, heating solutions of $\mathbf{2\text{-}d_B}$ or $\mathbf{2\text{-}d_P}$ to temperatures above 100°C in a sealed NMR tube, followed by cooling to 25°C, resulted in a statistical mixture of **2**, $\mathbf{2\text{-}d_2}$, $\mathbf{2\text{-}d_P}$, and $\mathbf{2\text{-}d_B}$. 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 $\mathbf{2\text{-}d_2}$ to **3**. The observation of HD in the statistical product mixture of H_2, D_2, 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 $^{31}P\{^1H\}$ NMR spectroscopy to monitor the formation of **3** from the loss of H_2 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 $3.5 \pm 0.6 \times 10^{-4}$ s^{-1} at 140°C. Eyring plots (fig. S3) over the temperature range 100° to 150°C provided the enthalpy of activation $\Delta H^{\neq} = 90 \pm 1$ kJ mol^{-1} and entropy of activation $\Delta S^{\neq} = -96 \pm 1$ J mol^{-1} 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 H_2 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 H_2 by **3** is intuitively thought to be initiated by the interaction of H_2 with B, that proton migration is more likely. This view is supported by the fact that **4** did not react with H_2.

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 % H_2, 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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29. Crystallographic parameters of **2** (numbers in parentheses are errors in the last significant digits): space group $P\bar{1}$, a = 10.9443(18) Å, b = 11.6829(19) Å, c = 13.617(2) Å, α = 72.560(2)°, β = 89.300(3)°, γ = 89.039(3)°, V = 1660.8(5) Å^3, data: 4782, variables: 469, R = 0.1291, R_w = 0.3280, goodness of fit: 1.001. Crystallographic parameters of **4**: space group $P\bar{1}$, a = 8.8328(14) Å, b = 11.0137(18) Å, c = 21.073(3) Å, α = 100.414(2)°, β = 95.590(2)°, γ = 111.122(2)°, V = 1851.1(5) Å^3, data: 6502, variables: 520, R = 0.0461, R_w = 0.1146, goodness of fit: 1.005.
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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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