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Facile Heterolytic Cleavage of Dihydrogen by Phosphines and Boranes

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Reactions of dihydrogen with transition metal complexes are a well-known aspect of organometallic chemistry and hydrogenation catalysis.[1−7] Analogous reactions of main group compounds are much less studied. Several examples involving main group element−H_2 reactions in low-temperature matrices have been reported in the literature.[8−10] While Sweany and co-workers have detected H_2 interactions with Lewis acids and bases as well as alkali halides in an argon matrix,[11−13] computational studies have probed the occurrence of dihydrogen bonds in the main group compounds.[14,15] More recently, Power and co-workers[16] reported the addition of H_2 to group 14 alkyne analogue compounds, affording a mixture of digermene, digermane, and primary germane products. On the other hand, phosphine−borane adducts of the form $R_2PH(BH_3)$ are known to thermally or catalytically eliminate H_2 to form cyclic and polymeric phosphinoboranes.[17−19] We[20] recently communicated the thermal liberation of H_2 from the phosphonium borate salt, $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)$, at temperatures above 100 °C, while the resulting product, $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$, adds H_2 at 25 °C to re-form the original salt. Mechanistic information regarding this reversible H_2 activation suggests that H_2 uptake occurs via interaction with the Lewis acidic B center followed by intramolecular proton migration to P. Given this finding, we sought simpler systems capable of such heterolytic cleavage of H_2. We now report the facile formation of phosphonium borates from the reaction of sterically demanding phosphines, boranes, and H_2. Steric congestion precludes quenching of reactivity via Lewis acid−base adduct formation allowing consecutive reactions of the Lewis acidic and Lewis basic centers with H_2.

Toluene solutions of stoichiometric mixtures of R_3P (R = *t*-Bu, $C_6H_2Me_3$) with $B(C_6F_5)_3$ were monitored by $^{31}P\{^1H\}$, ^1H, ^{11}B, and ^{19}F NMR spectroscopy. These experiments showed no evidence of the formation of Lewis acid−base adducts at 25 °C or on cooling to −50 °C. The absence of Lewis adduct formation is consistent with the sterically demanding nature of the phosphines R_3P (R = *t*-Bu, $C_6H_2Me_3$), which precludes coordination to the Lewis acidic B center or nucleophilic aromatic substitution at a *para*-carbon of $B(C_6F_5)_3$ as has been seen for $(C_6H_2Me_3)_2PH$.[20] It is noteworthy that solutions of $t\text{-}Bu_3P$ and $B(C_6F_5)_3$ are colorless, while those of $(C_6H_2Me_3)_3P$ and $B(C_6F_5)_3$ are violet in color (λ_{max} = 519 nm). The latter observation is thought to arise from π-stacking of electron-rich and electron-poor arene rings of the borane and phosphine. Interestingly, exposure of these phosphine/borane solutions to an atmosphere of H_2 at 1 atm pressure and 25 °C resulted in the quantitative formation of white precipitates **1** and **2**. NMR data for these products were consistent with the formulation as $[R_3PH][HB(C_6F_5)_3]$ (R = *t*-Bu **1**, $C_6H_2Me_3$ **2**)[21] (Scheme 1). The cations of these species exhibit ^{31}P resonances at 56.6 and −27.5 ppm for **1** and **2**, with P−H couplings of 454 and 480 Hz, respectively. In addition, the anion gives rise to a ^{11}B resonance at −25.5 ppm with a B−H coupling of 100 Hz. Moreover, the ^{19}F NMR chemical shift difference ($\Delta_{m,p}$) between the *ortho*- and *meta*-F atoms of the C_6F_5 fragments is consistent with the presence of a four-coordinate anionic boron center.[22] A crystallographic study of **1** showed disorder of the *t*-Bu groups of the cation. The chemically most reasonable model required the constraint of the C−C distances with the *t*-Bu groups. Nonetheless, the crystallographic data[23] confirmed the formulation based on spectroscopy (Figure 1). In the case of **2**, a preliminary solution confirmed the formulation, but poor crystal quality precluded a fully acceptable refinement.[23]

Scheme 1. Heterolytic Cleavage of H_2 by Phosphine and Borane

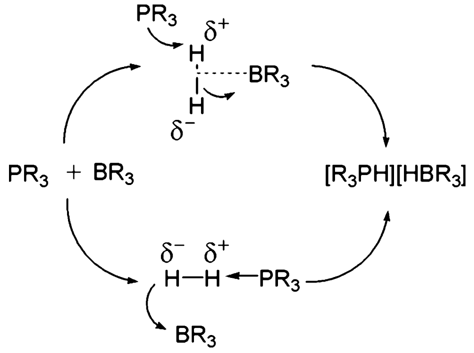
$$B(C_6F_5)_3 + PR_3 \xrightarrow[\text{1 atm, 25°C}]{H_2} [R_3PH][HB(C_6F_5)_3]$$

R = *t*Bu **1**, $C_6H_2Me_3$ **2**

$$BPh_3 + P\mathit{t}Bu_3 \xrightarrow[\text{1 atm, 25°C}]{H_2} [\mathit{t}Bu_3PH][HBPh_3]$$

3

Scheme 2. Possible Mechanisms for Heterolytic Cleavage of H_2 by Phosphine and Borane



The metric parameters determined for **1** are unexceptional. It is noted that the cations and anions pack such that the BH and PH

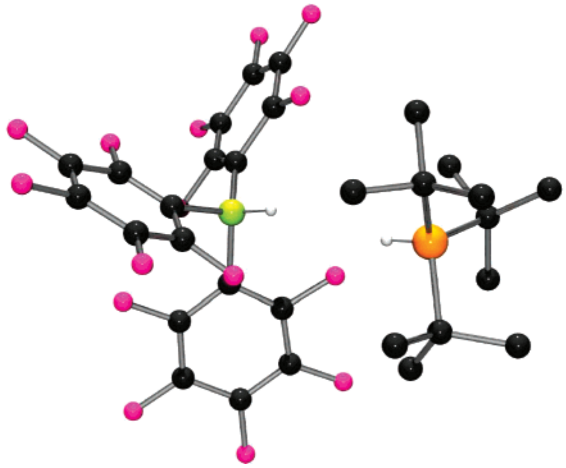


Figure 1. POV-ray drawing of **1**. Hydrogen atoms except for BH and PH are omitted for clarity. C, black; P, orange; F, pink; B, yellow-green; H, gray.

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units are oriented toward each other with the BH···HP approach being 2.75 Å, which is much larger than typical intermolecular H-bonding.[24] Despite this orientation in the solid state, heating of **1** or **2** in toluene solutions to 150 °C did not result in the loss of H_2. This stands in contrast to the $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)$ species, where an intramolecular proton migration process is proposed to account for the liberation of H_2 above 100 °C.[20] A solution of $(C_6H_2Me_3)_3P$ and $B(C_6F_5)_3$ in protio bromobenzene under 4 atm of D_2 in a sealable NMR tube was shaken and allowed to sit for several hours.[21] The ^{31}P NMR spectrum showed a triplet at -28.1 ppm ($J_{PD} = 74$ Hz), while the ^2D NMR spectrum gave rise to a doublet at 7.5 ppm and a broad singlet at 3.8 ppm, attributed to the PD and BD fragments, respectively. This affirms that the source of PH and BH is indeed dihydrogen. Compounds **1** and **2** are sensitive to H_2O, affording the phosphonium salt of the known anion $[R_3PH][(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$.[25]

In order to gain insight into the generality of the reaction, several phosphine/borane combinations were investigated. Attempts to effect analogous H_2 cleavage reactions employing $t\text{-}Bu_3P$ and BPh_3 resulted in the formation of **3** in 33% yield, although longer reaction times are required for H_2 activation, presumably due to the reduced Lewis acidity at B. The spectroscopy for **3** showed features similar to those of **1** for the cation, while the anion gave rise to a signal at -6.9 with a B$-$H coupling of 75 Hz in the ^{11}B NMR spectrum, supporting the formation of **3** as $[t\text{-}Bu_3PH][HBPh_3]$.[21] In contrast, reactions of $(C_6H_2Me_3)_3P$ and BPh_3, $(C_6F_5)_3P$ and $B(C_6F_5)_3$, or $t\text{-}Bu_3P$ and $BMes_3$ resulted in no reaction at 25 °C under an atmosphere of H_2. As well, reactions of Ph_3P and Me_3P with $B(C_6F_5)_3$ under H_2 at 25 °C gave rise to only the classical Lewis acid$-$base adduct $(R_3P)B(C_6F_5)_3$ (R = Ph, Me). These results support the view that reaction with H_2 occurs only under favorable electronic and steric conditions. Not only must the Lewis acidity/basicity be correctly matched in terms of cumulative strength to effect heterolytic cleavage of H_2, but steric constraints must be sufficient to preclude the quenching of the respective basicity and acidity via adduct formation.

Efforts to garner mechanistic insights were undertaken. Intuitively, by analogy to transition metal chemistry, one might anticipate that a side-on interaction of H_2 with the Lewis acid BR_3 ($R = C_6F_5$, C_6H_5) results in polarization of H_2, thus facilitating protonation of an approaching phosphine resulting in the formation of **1**$-$**3** (Scheme 2). Attempts to observe such a Lewis acid$-H_2$ interaction were undertaken by treatment by $B(C_6F_5)_3$ with higher pressures of H_2 (4 atm). Monitoring these mixtures by ^1H and ^{19}F NMR spectroscopy at temperatures as low as 190 K showed resonances attributable to free $B(C_6F_5)_3$. No other species[26] were observed, and thus this experimental evidence suggests that a borane$-H_2$ adduct is not stable. Nonetheless, it is noted that computational studies examined the existence of BH_5 and described this species as a weak $(\eta^2\text{-}H_2)BH_3$ adduct.[27−30] An alternative mechanism that warrants consideration involves the interaction of Lewis bases with H_2 (Scheme 2). In this regard, Sweany and coworkers[11] have demonstrated the formation of van der Waal complexes for a variety of Lewis bases including phosphines with H_2 in an argon matrix. Such interactions are thought to lead to polarization of H_2 via an end-on base$-H_2$ interaction involving lone pair donation to the σ^* orbital of H_2. Further experimental and computational investigations into the nature of this mechanism are underway.

In summary, the facile heterolytic cleavage of H_2 is readily achieved at room temperature by the cooperative action of Lewis acidic boranes and Lewis basic phosphines, where steric congestion precludes quenching of the acid and base via adduct formation. The reactivity and utility of this remarkably simple system for heterolytic cleavage of H_2 is the subject of ongoing study.

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Supporting Information Available: Materials and methods used in the study, and crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data in CIF format have been deposited with Cambridge database #630936.

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(26) Exposure of toluene solutions of $B(C_6F_5)_3$ in a sealable NMR tube to 4 atm high purity H_2 showed NMR signals attributable to free $B(C_6F_5)_3$ and a lesser amount of $(H_2O)B(C_6F_5)_3$, which was confirmed by independent generation. See: Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *112*, 10581. Lesser amounts of $(H_2O)B(C_6F_5)_3$ were also observed even when the H_2 was dried with a column of dry-rite and molecular sieves and two in-stream cold traps. These observations are consistent with the ability of borane to scavenge trace amounts of water in the absence of other donors.
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