

# Dihydrogen Activation with $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ : A Chemically Competent Indirect Mechanism via in Situ-Generated $p\text{-}t\text{Bu}_2\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2$

Adam J. V. Marwitz, Jason L. Dutton, Lauren G. Mercier, and Warren E. Piers\*

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

Supporting Information

**ABSTRACT:** A chemically competent indirect pathway for the activation of dihydrogen by the nonmetal Lewis acid/Lewis base pair  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  is described. The reaction between  $t\text{Bu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  produces  $[t\text{Bu}_3\text{PH}]^+[\text{F}(\text{C}_6\text{F}_5)_2]^-$  and the known phosphinoborane  $p\text{-}t\text{Bu}_2\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2$  (**1- $t\text{Bu}$** ) with elimination of isobutylene. At 1:1 stoichiometry, **1- $t\text{Bu}$**  is produced rapidly in detectable quantities and can act as a catalyst for the formation of  $[t\text{Bu}_3\text{PH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$  from  $t\text{Bu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  in the presence of  $\text{H}_2$ . The extent to which this indirect path competes with the direct path is explored.

Research into the activation of dihydrogen<sup>1,2</sup> and other nonpolar bonds<sup>3,4</sup> by non-transition-metal systems has reached a crescendo of activity after recent discoveries in which Lewis acid/Lewis base pairs that do not form traditional adducts were observed to heterolytically cleave dihydrogen under ambient conditions.<sup>5,6</sup> The first such system was the linked phosphinoborane **1-Mes**<sup>7</sup> (Chart 1), which is converted rapidly (<5 min) to the corresponding phosphonium borate zwitterion upon exposure to 1 atm  $\text{H}_2$ .

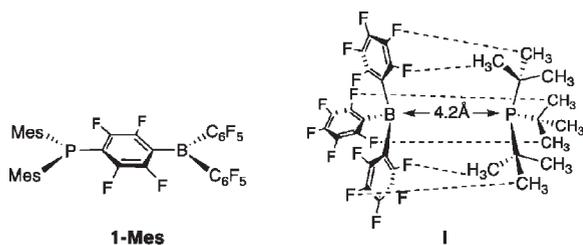
Since then, several other systems have been developed,<sup>8–10</sup> including a much studied pairing of  $t\text{Bu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ ,<sup>11</sup> two commercially available reagents that split hydrogen to form the ion pair  $[t\text{Bu}_3\text{PH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ . Trimesitylphosphine is also an able partner in this chemistry; furthermore,  $\text{B}(\text{C}_6\text{F}_5)_3$  has been used in combination with a variety of other bulky bases, notably imines,<sup>12</sup> to bring about metal-free imine hydrogenations via reactions related to the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilylation of carbonyl functions<sup>4</sup> and imines.<sup>13</sup> The term “frustrated Lewis pair” has been introduced to describe these bond-activating systems.<sup>5</sup>

Despite the facility of H–H bond cleavage by these systems and their obvious utility, there is surprisingly little experimental

detail available concerning the intimate or even stoichiometric mechanism by which the  $\text{H}_2$  activation takes place. Qualitatively, the rates in these  $\text{R}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  systems appear to be lower<sup>11</sup> than that observed for **1-Mes**,<sup>7</sup> but no serious comparative kinetic studies have been reported. What we do know stems mainly from theoretical treatments of these important reactions. For compound **1-Mes**, addition of  $\text{H}_2$  to the B–C bond of the  $\text{PR}_2$ -functionalized aryl group via a side-on  $\text{H}_2$  adduct of the Lewis acidic boron center, followed by a series of 1,2-hydrogen shifts, was proposed initially<sup>7</sup> and has been shown computationally to be an energetically feasible pathway.<sup>14</sup> However, the computed barriers are too high to account for the reported rates of this reaction, which occurs rapidly even at temperatures below 0 °C. In the  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  system, however, it is thought that an  $\eta^2\text{-H}_2$  adduct is not involved;<sup>15</sup> rather, it has been proposed that the phosphine and borane form a loosely associated “encounter complex”<sup>16</sup> that is stabilized by several weak  $\text{H}\cdots\text{F}$  interactions and dispersion forces (I in Chart 1), creating a pocket in which the  $\delta^-$  charge on the phosphine and the  $\delta^+$  charge on boron generate an electric field capable of polarizing  $\text{H}_2$  to the extent that bond cleavage is facile.<sup>15</sup> A related mechanism for the linked system **1-Mes** has subsequently been probed and found to be more consistent with experimentally observed rates.<sup>17</sup> Thus, there is substantial computational support for the encounter-complex mechanism. However, to the best of our knowledge, despite the reasonably substantial computed minima (–10 to –13 kcal mol<sup>–1</sup>) for such entities, all attempts to date to observe them via NMR spectroscopy have failed.

Although solutions of 1:1 mixtures of  $t\text{Bu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  have been reported to be colorless,<sup>11</sup> we observed that when very dry solvents (toluene or  $\text{CH}_2\text{Cl}_2$ ) and reagents<sup>18</sup> were employed, these solutions exhibited a pale-yellow color. Postulating that the color may have arisen from the elusive encounter complex, we endeavored to study these solutions by UV–vis spectroscopy in both toluene and  $\text{CH}_2\text{Cl}_2$ . In order to study more concentrated solutions, a 1 mm path length cuvette was employed. Control spectra established the absorption profiles of free  $t\text{Bu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ , which showed that neither absorbs above 365 nm; the spectrum of  $\text{B}(\text{C}_6\text{F}_5)_3$  agreed with that reported previously ( $\lambda_{\text{max}} = 303$  nm).<sup>19</sup> In mixtures, however, a weak band with  $\lambda_{\text{max}} = 373$  nm appeared on the shoulder of the main absorption band for  $\text{B}(\text{C}_6\text{F}_5)_3$ , and we ascribe this band to the species that imbues these solutions with the pale-yellow color (see Figure S1 in the Supporting Information). In a scenario in which this species is the encounter complex, the relative intensity of this band would be expected to exhibit a monotonic concentration dependence, since higher

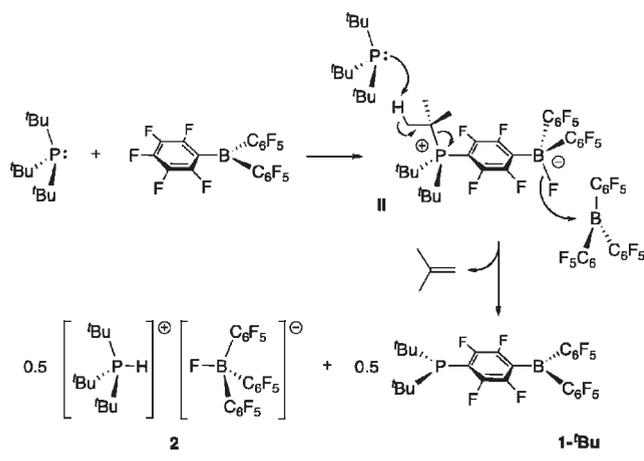
Chart 1



Received: April 7, 2011

Published: June 08, 2011

Scheme 1

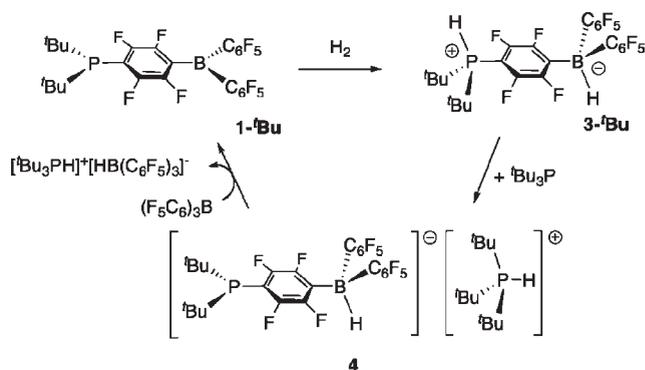


concentrations should favor its formation. This is a phenomenon that we did *not* observe in a reproducible way. Furthermore, using time-dependent density functional theory (DFT) methods, we computed the UV–vis spectrum of the encounter complex using published coordinates<sup>16</sup> and did not find evidence for a band that is red-shifted relative to the computed spectrum of free  $B(C_6F_5)_3$ .

In a further effort to favor formation of the encounter complex, 30 mg of  $B(C_6F_5)_3$  (0.06 mmol) was dissolved in 200 mg of liquid  $tBu_3P$  (1.0 mmol). An immediate color change to dark yellow was observed upon mixing of the two reagents; the borane dissolved completely in the phosphine, but soon after, colorless crystals began to deposit from the yellow-orange mixture. After several hours, these crystals were washed with cold toluene and collected; an X-ray crystallographic analysis of a single crystal from this batch showed it to be the phosphonium fluoroborate  $[tBu_3PH]^+[FB(C_6F_5)_3]^-$  (**2**); an ORTEP diagram of the salt (Figure S2) and crystal and metrical data are given in the Supporting Information. Multinuclear NMR spectroscopy confirmed its identity; in particular, the broad signal at  $-188$  ppm in the  $^{19}F$  NMR spectrum that integrated to one fluorine is consistent with the formation of the fluoroborate anion.

The demands of a balanced chemical equation imply that in addition to **2**, isobutylene and the known phosphinoborane  $1-tBu$ <sup>20</sup> must also be produced. Thus, the maximum yield of **2** in the above experiment is 50%; we recovered a yield of 48%, with the remainder presumably lost in the isolation procedure. Accordingly, examination of a concentrated 1:1  $tBu_3P/B(C_6F_5)_3$  mixture by multinuclear NMR spectroscopy confirmed the presence of  $1-tBu$ , with a characteristic doublet of doublets at 25 ppm in the  $^{31}P\{^1H\}$  NMR spectrum being the most convincing evidence.<sup>20</sup> Compounds **2** and  $1-tBu$  were formed in a 1:1 ratio, and with small amounts of other fluorine-containing species, in addition to the starting materials, were also present in these samples. Furthermore, when the reaction was conducted in a sealed NMR tube, the presence of free isobutylene was detected in the  $^1H$  NMR spectrum (4.74 and 1.59 ppm). The expulsion of isobutylene from *tert*-butylphosphonium salts has been observed in other recent studies.<sup>20,21</sup> Finally, when a yellow  $tBu_3P/B(C_6F_5)_3$  mixture was examined by MALDI–TOF mass spectrometry, a molecular-ion peak for  $1-tBu$  was clearly observed in the mass spectrum in addition to peaks associated with **2** and the Lewis pair components.

Scheme 2

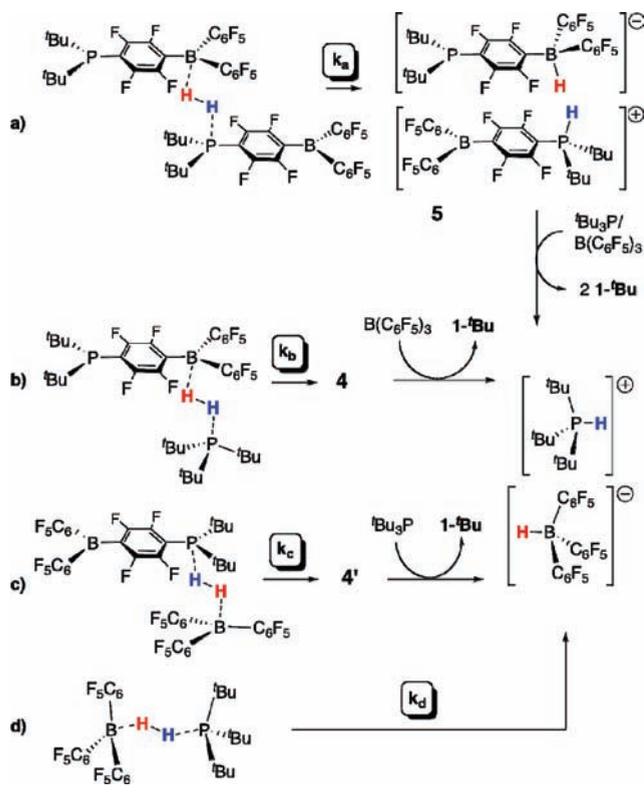


Since the reported UV–vis spectrum of  $1-tBu$  is dominated by an absorption with  $\lambda_{max} = 373$  nm,<sup>20</sup> it is clear that the yellow color observed in dilute (and concentrated) mixtures of  $tBu_3P$  and  $B(C_6F_5)_3$  is due to  $1-tBu$ , which likely is formed via the chemistry depicted in Scheme 1. It is already well-known that other phosphines react with  $B(C_6F_5)_3$  via attack of the phosphine at a *p*-fluoro group, resulting in the formation of zwitterionic phosphonium fluoroborates. To our knowledge, the precise species shown here (**II**) has not been previously reported, but it may be responsible for the minor unassigned peaks in the  $^{19}F$  NMR spectra that we recorded for these samples. In the presence of a large excess of  $tBu_3P$  and  $B(C_6F_5)_3$ , the elements of H–F are rapidly removed from **II** by deprotonation of a *tert*-butyl group and abstraction of a fluoride to produce **2** and  $1-tBu$ , as shown; this also accounts for the observed isobutylene. We found that the production of detectable amounts of  $1-tBu$  occurs essentially upon mixing of  $tBu_3P$  and  $B(C_6F_5)_3$  in both toluene and  $CH_2Cl_2$  solutions.

The presence of  $1-tBu$  in solutions of  $tBu_3P$  and  $B(C_6F_5)_3$  raises significant questions concerning the mechanism by which this particular Lewis pair activates dihydrogen. For example, as mentioned above, it has been reported that **1-Mes** activates  $H_2$  more rapidly than do solutions of  $tBu_3P$  and  $B(C_6F_5)_3$ . It is therefore conceivable that  $1-tBu$  is a catalyst for the formation of  $[tBu_3PH]^+[HB(C_6F_5)_3]^-$  via the pathway shown in Scheme 2. In such a scenario,  $H_2$  addition to  $1-tBu$  generated the known linked phosphonium hydrideborate  $3-tBu$ .<sup>20</sup> From there, deprotonation of the phosphonium moiety by free  $tBu_3P$  likely would precede hydride abstraction, since the phosphonium center in  $3-tBu$  is more acidic than  $[tBu_3PH]^+$ , while it has been shown that the boron centers in phosphonium boranes are stronger Lewis acids than that in  $B(C_6F_5)_3$ .<sup>20,22,23</sup> Indeed, the stoichiometric reaction of separately prepared  $3-tBu$  and  $tBu_3P$  led rapidly (essentially upon mixing) to ion pair **4**, as determined by NMR spectroscopy (see the Supporting Information). In particular, a new doublet for the  $[tBu_3PH]^+$  cation at 5.25 ppm ( $^1J_{PH} = 433$  Hz) and two characteristic signals at 59.9 and 20.9 ppm in the  $^{31}P$  NMR spectrum are indicative of formation of **4** from  $3-tBu$ . Conversely, a separate experiment showed that  $3-tBu$  does not surrender hydride to  $B(C_6F_5)_3$ . However, treatment of **4** with  $B(C_6F_5)_3$  generated  $[tBu_3PH]^+[HB(C_6F_5)_3]^-$  and  $1-tBu$ , again essentially upon mixing.

These experiments certainly demonstrate the chemical competency of such a phosphinoborane-catalyzed pathway for hydrogen splitting by the  $tBu_3P/B(C_6F_5)_3$  Lewis pair. However,

Scheme 3



establishing the kinetic competency of the pathway depicted in Scheme 2, as opposed to direct activation of H<sub>2</sub> by <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, is nontrivial because production of 1-<sup>t</sup>Bu occurs with great facility upon mixing of the phosphine and borane. In our hands, it was not possible to generate solutions of <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> that did not contain at least a small amount (1–5%) of 1-<sup>t</sup>Bu.

The situation is further complicated by the possibility that encounter complexes between 1-<sup>t</sup>Bu and <sup>t</sup>Bu<sub>3</sub>P or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> may also be involved in activating hydrogen, providing alternate pathways for the generation of the observed product [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>. Thus, four possible H<sub>2</sub> activation steps may be envisioned, as depicted in Scheme 3. Of these possible paths, three of the four (a–c) represent reactions that are catalytic in 1-<sup>t</sup>Bu, while the fourth (d) is the direct path. In path a, activation of H<sub>2</sub> by 1-<sup>t</sup>Bu via the encounter-complex path would yield ion pair 5 as the kinetic product; in the absence of <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, this would likely disproportionate to 1-<sup>t</sup>Bu/3-<sup>t</sup>Bu,<sup>24</sup> but in the presence of an excess of the Lewis pair, it would rapidly be converted to product based on the results shown in Scheme 2. The kinetic product of path b would in fact be ion pair 4, which would be rapidly converted to product in the presence of borane (see above), and it would also be expected that the ion pair [*p*-(F<sub>5</sub>C<sub>6</sub>)<sub>2</sub>B–C<sub>6</sub>F<sub>4</sub>–P(H)<sup>t</sup>Bu<sub>2</sub>]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> (4') formed in path c would also be rapidly converted to product and/or 3-<sup>t</sup>Bu once formed.

We attempted to probe the relative importance of the catalyzed paths versus the direct path by a semiquantitative investigation of the reactions of solutions of 1-<sup>t</sup>Bu (with and without added phosphine or borane) and the unlinked pair <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (prepared in such a way as to minimize production of 1-<sup>t</sup>Bu) with H<sub>2</sub> under the same conditions. Thus, separate

0.07 M C<sub>6</sub>D<sub>5</sub>Br solutions of 1:1 <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and 1-<sup>t</sup>Bu were prepared, degassed, exposed to 4 atm H<sub>2</sub>, and warmed to room temperature, and the reactions were monitored by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopy. In the first sample, production of [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> was complete in less than 10 min after exposure to H<sub>2</sub>; traces of 1-<sup>t</sup>Bu were detected in the baseline of the spectra. This reaction is thus very rapid and does not require several hours to reach completion as initially reported.<sup>11</sup> In the reaction of pure 1-<sup>t</sup>Bu with H<sub>2</sub>, the only species present in the <sup>31</sup>P NMR spectra were the starting material and the expected zwitterionic product of H<sub>2</sub> addition, 3-<sup>t</sup>Bu; this process took ~120 min to reach full conversion. Thus, it appears that addition of hydrogen to 1-<sup>t</sup>Bu in the absence of <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is slower than splitting of H<sub>2</sub> by <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> when only a trace of 1-<sup>t</sup>Bu is present (i.e., to a first approximation, k<sub>d</sub> > k<sub>a</sub>).

The comparatively slow addition of H<sub>2</sub> to 1-<sup>t</sup>Bu that we observed occurred in the absence of <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. However, in the reaction of the unlinked pair with H<sub>2</sub>, there was always a small amount of 1-<sup>t</sup>Bu present, which implies that the scenarios outlined in Scheme 3b,c cannot be ignored. Significantly, when 1-<sup>t</sup>Bu was mixed with 1 equiv of <sup>t</sup>Bu<sub>3</sub>P in the absence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> under the same conditions as described above and then exposed to 4 atm H<sub>2</sub>, ion pair 4 (Scheme 2) was formed almost immediately (within 5 min) and quantitatively. The analogous experiment aimed at probing Scheme 3c, wherein 1-<sup>t</sup>Bu was mixed with 1 equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and treated with H<sub>2</sub>, resulted in addition of H<sub>2</sub> to form 3-<sup>t</sup>Bu at a rate consistent with that observed in the absence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

In an effort to further delineate the relative rates of these reactions, the rapid processes were probed using the following procedure. A solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.0488 M in toluene) was degassed and exposed to H<sub>2</sub> (1 atm); a separate solution of <sup>t</sup>Bu<sub>3</sub>P (also 0.0488 M in toluene) that had been degassed and saturated with H<sub>2</sub> was added in one portion to the solution of borane under a strong flow of H<sub>2</sub> with vigorous stirring. Precisely 1 min after addition, the reaction was exposed to vacuum and evaporated to dryness; the resulting residue was assayed by <sup>1</sup>H NMR spectroscopy using hexamethylbenzene as an internal standard, and it was found that 38 ± 2% conversion to [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> had occurred. A similar experiment employing a mixture of 1-<sup>t</sup>Bu and <sup>t</sup>Bu<sub>3</sub>P, each at 0.0488M, showed a similar extent of conversion to the ion pair (35 ± 2%) after one minute. Thus, the rates of H<sub>2</sub> addition to these two frustrated Lewis pairs appear to be quite similar (i.e., k<sub>d</sub> ≈ k<sub>b</sub>), despite<sup>25</sup> the lower Lewis acid strength of the borane center in 1-<sup>t</sup>Bu in comparison with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. When 20 mol % 1-<sup>t</sup>Bu was added to the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> solution, the conversion to [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> after 1 min increased to 54 ± 2%. This increase was not large enough to indicate the dominance of a catalyzed path of H<sub>2</sub> addition to the Lewis pair <sup>t</sup>Bu<sub>3</sub>P and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, but it does suggest that such a path could be competitive with direct addition via the encounter complex I under conditions where significant quantities of 1-<sup>t</sup>Bu are present.

In conclusion, although the Lewis pair consisting of <sup>t</sup>Bu<sub>3</sub>P and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> do not form a classical Lewis acid/base adduct, the partners do react in a facile process via coordination of the <sup>t</sup>Bu<sub>3</sub>P to one of the para carbons of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This occurs because the two essentially degenerate LUMO+1 orbitals are situated mostly on the para carbons (see Figure S3). This triggers the formation of 1-<sup>t</sup>Bu, which can serve as a catalyst for addition of H<sub>2</sub> to the <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pair via a chemically competent sequence of reaction steps. On the basis of semiquantitative kinetic

experiments, it appears that direct addition is likely still the dominant reaction coordinate, but under certain conditions, the 1-<sup>t</sup>Bu catalyzed path may constitute a significant fraction of the path by which [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> is formed. Whether or not this mechanistic scenario is specific to the <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pair remains an open question, and we are currently investigating the feasibility of this alternate path in other Lewis base/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pairs.<sup>10,26,27</sup> Irrespective of the generality of this indirect mechanism, the results described here show that despite the seeming simplicity of the reactions observed, the mechanistic picture is complex and requires further study.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Full experimental details, UV–vis spectra, X-ray crystallographic data for **2** (CIF), and DFT computational output. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

wpiers@ucalgary.ca

## ■ ACKNOWLEDGMENT

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, an NSERC Graduate Scholarship (L.G.M.), and an Alberta Innovates Studentship (L.G.M.). The authors thank the reviewers for thoughtful and constructive comments.

## ■ REFERENCES

- (1) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439–441.
- (2) Spikes, G. H.; Fettingner, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.
- (3) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441.
- (4) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090–3098.
- (5) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
- (6) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535–1539.
- (7) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126.
- (8) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074.
- (9) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117–14119.
- (10) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7428–7432.
- (11) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.
- (12) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701–1703.
- (13) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921–3923.
- (14) Rajeev, R.; Sunoj, R. B. *Chem.—Eur. J.* **2009**, *15*, 12846–12855.
- (15) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 1402–1405.
- (16) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 2435–2438.
- (17) Guo, Y.; Li, S. *Inorg. Chem.* **2008**, *47*, 6212–6219.
- (18) Beringhelli, T.; Maggioni, D.; D'Alfonso, G. *Organometallics* **2001**, *20*, 4927–4938.
- (19) Chojnowski, J.; Rubinsztajn, S.; Cella, J. A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kazmierski, K. *Organometallics* **2005**, *24*, 6077–6084.
- (20) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2007**, 3407–3414.
- (21) Jiang, C.; Blacque, O.; Fox, T.; Berke, H. *Dalton Trans.* **2011**, *40*, 1091–1097.
- (22) Chiu, C.-W.; Kim, Y.; Gabbai, F. P. *J. Am. Chem. Soc.* **2009**, *131*, 60–61.
- (23) Kim, Y.; Gabbai, F. P. *J. Am. Chem. Soc.* **2009**, *131*, 3363–3369.
- (24) Indeed, separate syntheses of the linked hydridoborate and phosphonium ions as their [<sup>t</sup>Bu<sub>3</sub>PH] and [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] salts, respectively, showed that their combination results in immediate disproportionation. This is a feature of the chemistry of hydrogen addition to compounds **1** that was not anticipated by the theoretical treatment of Guo and Li<sup>17</sup> and may account for the complex kinetic behavior observed for this reaction.<sup>5,7</sup>
- (25) Rokob, T. A.; Hamza, A.; Pápai, I. *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710.
- (26) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001–6003.
- (27) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433–7437.