**$H_2$ Activation**

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# Heterolytic Dihydrogen Activation by a Frustrated Carbene–Borane Lewis Pair**

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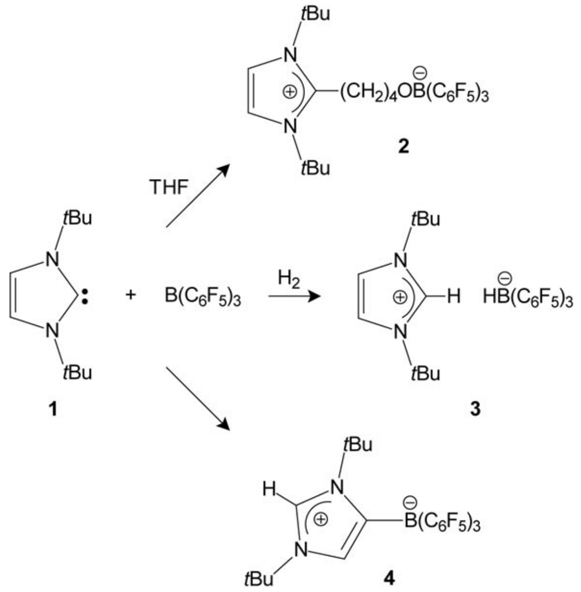
The Lewis acid–base concept is fundamental for the understanding and the prediction of chemical structure and reactivity.[1] For instance, boranes ($BR_3$) and phosphines ($PR'_3$) represent prototypical Lewis acids and bases, respectively, and as such, they are prone to form stable donor–acceptor adducts[2,3] in which the unshared pair of the base forms a covalent bond with the vacant orbital of the acid. Steric factors can suppress this inherent behavior, leading to so-called "frustrated Lewis pairs" (FLPs).[4] Only recently, the group of D. W. Stephan was able to demonstrate that FLPs consisting of boranes, in particular tris(pentafluorophenyl)borane, $B(C_6F_5)_3$,[5] and sterically demanding phosphines are excellent non-metallic systems for the activation of small molecules such as dihydrogen, olefins, and tetrahydrofuran under mild conditions.[6–8] Activation of dihydrogen proceeds heterolytically, cleanly affording phosphonium borate salts of the type $[R'_3PH][HBR_3]$.[6b,c] For the $P(t\text{Bu})_3/B(C_6F_5)_3$ pair, a recent theoretical study has arrived at a novel mechanistic proposal that involves the preorganization of the donor–acceptor site, providing the possibility of bifunctional cooperativity for a synergistic interaction with an incoming dihydrogen molecule.[9] There is a striking similarity between electron-rich organophosphines and nucleophilic carbenes of the imidazolin-2-ylidene type in terms of their ligand properties,[10] and this prompted us to attempt the development of novel carbene-containing FLP systems and to study their use in small molecule activation. It should be emphasized that imidazolin-2-ylidenes alone and related di(amino)carbenes are inert towards dihydrogen,[11] whereas acyclic and cyclic (alkyl)(amino)carbenes undergo oxidative addition of dihydrogen at the carbene carbon atom.[12]

The combination of 1,3-di-*tert*-butylimidazolin-2-ylidene (**1**) with tris(pentafluorophenyl)borane was chosen as an initial carbene–borane FLP, and mixing of these two compounds in THF afforded the imidazolium–borate zwitterion **2** as a white solid in almost quantitative yield (Scheme 1). The formation of **2** can be rationalized by nucleophilic attack of **1** at the Lewis acid–base adduct THF–$B(C_6F_5)_3$, effecting ring-opening of the THF ligand in a similar fashion to that described for the formation of phosphonium borates from tris(pentafluorophenyl)borane and sterically demanding phosphines.[8] Incorporation of a bridging $(CH_2)_4O$ moiety was indicated by the observation of four methylene resonances at 3.40, 3.23, 1.93, and 1.67 ppm in the $^1$H NMR spectrum and at 61.3, 31.8, 28.5, and 27.6 ppm in the $^{13}$C NMR spectrum. The $^{11}$B NMR resonance at −2.8 ppm is identical to that observed for $[Mes_2PH(CH_2)_4OB(C_6F_5)_3]$.[8] The zwitterionic nature of **2** was also confirmed by an X-ray crystal structure analysis,[20] and the molecular structure has C−N bond lengths (C1−N1 1.345(2) Å, C1−N2 1.350(2) Å) and an N1-C1-N2 angle (107.85(15)°) that are typical for imidazolium cations (Figure 1).[13] The ring-opened THF results in an O−B bond of 1.456(2) Å and a C1−C12 bond of 1.498(2) Å.



*Scheme 1.* Reactions of the frustrated Lewis pair (FLP) **1**/$B(C_6F_5)_3$.

The reactivity of the Lewis pair **1**/$B(C_6F_5)_3$ suggested the presence of frustration, as the use of sterically less-demanding carbenes is expected to give conventional carbene–borane adducts with substitution and liberation of the THF ligand.[14,15] Therefore, it was expected that **1**/$B(C_6F_5)_3$ would represent a viable system for the activation of dihydrogen. Indeed, purging of a toluene solution containing equimolar amounts of **1** and $B(C_6F_5)_3$ with $H_2$ at 20 °C resulted in the instantaneous formation of a white precipitate, and after stirring for 10 min, the imidazolium borate salt **3** could be

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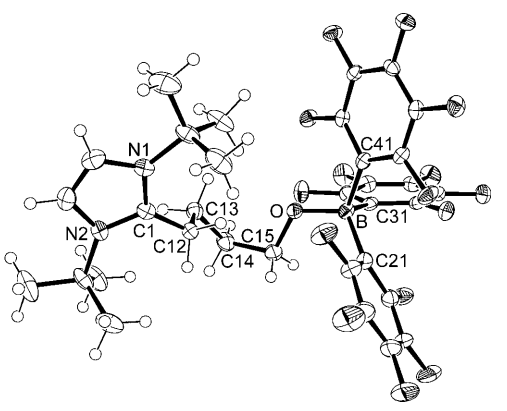

*Figure 1.* ORTEP of **2**, with thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: C1–N1 1.345(2), C1–N2 1.350(2), C1–C12 1.498(2), B–O 1.456(2), C15–O 1.417(2); N1-C1-N2 107.85(15), O-B-C41 107.13(14), O-B-C31 112.89(14), O-B-C21 108.42(14).

isolated by filtration in 82% yield (Scheme 1). In the $^1$H NMR spectrum, signals pertaining to the cation are observed at 8.10 ppm and at 7.37 ppm for the two types of NCH hydrogen atoms, along with a singlet at 1.57 ppm for the *tert*-butyl hydrogen atoms, whereas the anion gives rise to a broad quartet at 3.58 ppm with $^1J(^1H,^{11}B)$ of circa 100 Hz. The $^{11}$B NMR resonance is observed at −25.2 ppm, and the $^{19}$F NMR spectrum shows three resonances at −132.3, −162.9, and −166.0 ppm for the *ortho*, *para*, and *meta* fluorine atoms, respectively.

Single crystals of **3** suitable for X-ray crystal structure determination[20] were obtained from $CH_2Cl_2$/pentane solution, and the asymmetric unit of **3** is shown in Figure 2. The structural parameters are in full agreement with the presence of an imidazolium cation and a tetrahedral $[HB(C_6F_5)_3]$ anion with the C-B-C angles ranging from 110.48(15)° to 113.63(15)°. Unlike the BH···HP contact of 2.75 Å observed for the salt $[(t\mathrm{Bu})_3PH][HB(C_6F_5)_3]$,[6b] the corresponding C–H and B–H units in **3** are not oriented towards one another. Instead, all C–H ring hydrogen atoms display C–H···F contacts ranging from 2.50 to 2.62 Å, whereas the B–H hydrogen atom is symmetrically capped by a *tert*-butyl group, with BH···HC contacts of 2.50, 2.55, and 2.57 Å.

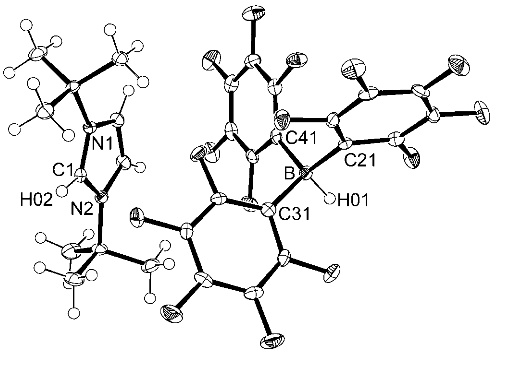

*Figure 2.* ORTEP diagram of **3**, with thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: C1–N1 1.331(2), C1–N2 1.332(2), B–H01 1.18(2), C1–H02 0.95(2); N1-C1-N2 109.26(16), C21-B-C31 110.48(15), C21-B-C41 113.63(15), C41-B-C31 112.38(16).

The limitations of the FLP system **1**/$B(C_6F_5)_3$ came to light through the observation that initially yellow solutions of **1** and $B(C_6F_5)_3$ turn colorless in toluene, and completely lose their reactivity towards dihydrogen within two hours at room temperature. Evaporation of the solvent and suspension in hexane afforded a white solid in 95% yield, which was characterized by elemental analysis and mass spectrometry, clearly indicating the formation of a 1:1 carbene–borane adduct. Recrystallization from $CHCl_3$/pentane solution afforded single crystals suitable for an X-ray diffraction analysis,[20] and the molecular structure reveals the formation of the adduct **4**, which contains an "abnormal" carbene ligand (Figure 3).[16] The $B(C_6F_5)_3$ moiety is attached to the 4 position of the imidazole heterocycle, which involves migration of the corresponding hydrogen atom to the former carbene carbon atom. Accordingly, the five-membered ring features structural parameters that are typical for complexes containing abnormal carbene ligands of the imidazolium-4-yl type.[16] The B–C2 distance is 1.649(3) Å and is almost identical to that found in the normal adduct between tris(pentafluorophenyl)borane and the sterically less-encumbered carbene 1,3,4,5-tetramethylimidazolin-2-ylidene.[15] The *tert*-butyl group at N1 is interlocked with two $C_6F_5$ rings, suggesting that the rotation around the B–C axis might be severely hindered. Indeed, the $^{19}$F NMR spectrum exhibits six signals each for the *ortho* and *meta* fluorine atoms and three signals for the *para* fluorine atoms, which can be explained by hindered rotation around all four B–C bonds, rendering the 15 fluorine atoms inequivalent at room temperature on the NMR time scale. In agreement with the abnormal binding mode, the $^1$H and $^{13}$C NMR spectra indicate the presence of two different *tert*-butyl and C–H groups.

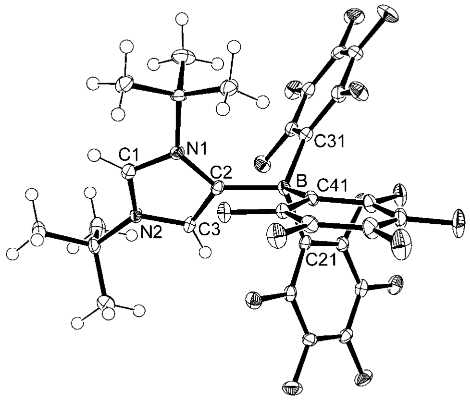

*Figure 3.* ORTEP diagram of **4**, with thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: B–C2 1.649(3), C1–N1 1.336(3), C2–N1 1.414(3), C1–N2 1.321(3), C3–N2 1.371(3), C2–C3 1.350(3); C1-N1-C2 108.62(19), C1-N2-C3 106.92(19), N1-C1-N2 110.0(2), C3-C2-N1 103.76(19), C2-C3-N2 110.7(2), C2-B-C41 115.10(18), C2-B-C31 108.35(18), C2-B-C21 107.99(18).

To gain further insight into the reactivity of the FLP system **1**/$B(C_6F_5)_3$, we carried out a series of DFT calculations,[20] initially applying the popular B3LYP functional. In contrast to calculations reported for the $P(tBu)_3/B(C_6F_5)_3$ pair, we were able to identify a covalently bound adduct **A** as a minimum on the B3LYP potential energy surface (PES), with a B–C bond length of 1.74 Å, which is higher in energy ($\Delta E = +2.3$ kcal mol$^{-1}$) with respect to the starting materials **1** and $B(C_6F_5)_3$ (Figure 4). As it has been shown that B3LYP is unable to properly describe medium-range dispersion interactions,[17] which also significantly contribute to the overall binding energy in related phosphine/$B(C_6F_5)_3$ adducts,[3d] the M05-2X functional developed by Truhlar, which better describes noncovalent interactions, was then used,[17b] resulting in an appreciably stronger stabilization of the carbene–borane adduct **A** ($\Delta E = -23.8$ kcal mol$^{-1}$, d(B–C) = 1.71 Å). Furthermore, a relaxed PES scan with respect to the B–C distance allowed us to identify a second minimum **B** at d(B–C) = 4.51 Å with an association energy of $\Delta E = -10.9$ kcal mol$^{-1}$ (Figure 4), which represents a weakly bound adduct stabilized by a combination of C–H···F hydrogen bonds and C–H···π interactions in a similar fashion to that described for the $P(tBu)_3/B(C_6F_5)_3$ system (see the Supporting Information for a detailed presentation of the calculated molecular structures).[20]

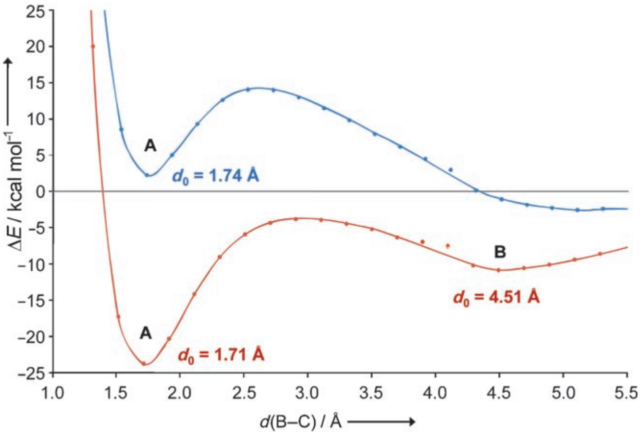

***Figure 4.*** Potential energy curves derived at B3LYP/6-311G(d,p) (blue) and M05-2X/6-311G(d,p) (red) levels for the interaction between 1,3-di-*tert*-butylimidazolin-2-ylidene (**1**) and tris(pentafluorophenyl)borane.

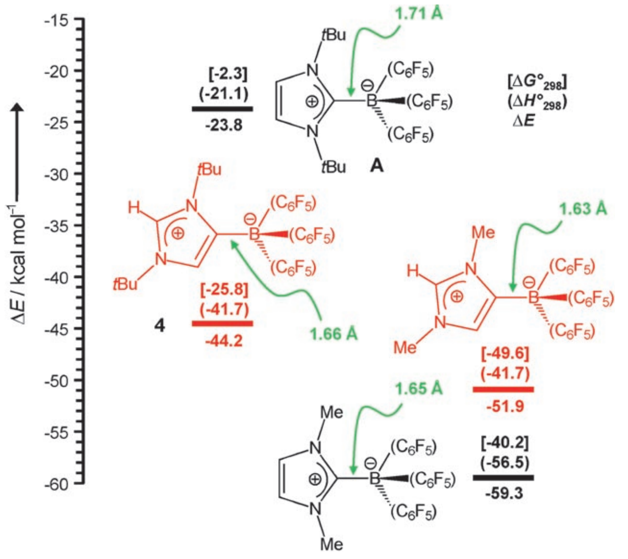

***Figure 5.*** Relative energies of normal (black) and abnormal (red) carbene–borane adducts. Values correspond to $\Delta E$ = zero-point uncorrected M05-2X/6-311G(d,p) electronic energies, $\Delta H^\circ_{298}$ = enthalpies at 298 K (in round brackets), and $\Delta G^\circ_{298}$ = Gibbs free energies at 298 K [in square brackets].

Although the calculations predict the formation of a stable adduct $\mathbf{1}/B(C_6F_5)_3$ (**A**), partial dissociation of this complex in solution is very likely at room temperature, as the Gibbs free energy of $\Delta G^\circ_{298} = -2.3$ kcal mol$^{-1}$ indicates only a marginally exergonic reaction and an almost complete compensation of its exothermic nature by entropy loss (Figure 5). Optimization of the structure of the abnormal adduct **4** furnishes structural parameters that are in good agreement with those experimentally observed by X-ray diffraction (see above); for example, $d(\text{B–C})_{\text{calc}} = 1.66$ Å and $d(\text{B–C})_{\text{exp}} = 1.649(3)$ Å. The formation of **4** is calculated to be significantly more exothermic ($\Delta E = -44.2$ kcal mol$^{-1}$), which confirms the experimental observation that this adduct is formed irreversibly with complete loss of reactivity towards dihydrogen. For comparison, the corresponding normal and abnormal Lewis acid–base adducts consisting of the sterically less demanding 1,3-dimethylimidazolin-2-ylidene and tris(pentafluorophenyl)borane were also calculated, revealing that both the normal ($\Delta E = -59.3$ kcal mol$^{-1}$) and abnormal adduct ($\Delta E = -51.9$ kcal mol$^{-1}$) are significantly more stable with respect to their di-*tert*-butyl congeners (Figure 5). In contrast to the frustrated system $\mathbf{1}/B(C_6F_5)_3$, the formation of the normal dimethylcarbene–borane adduct is highly exergonic ($\Delta G^\circ_{298} = -40.2$ kcal mol$^{-1}$), and this combination can thus clearly be classified as non-frustrated. It should be noted that the corresponding B–C(carbene) distance of 1.65 Å is virtually identical to the value that was reported for the closely related 1,3,4,5-tetramethylimidazolin-2-ylidene-tris(pentafluoro)borane complex (1.6407(16) Å).[15]

In analogy to the reaction pathway theoretically derived for the heterolytic cleavage of dihydrogen with $P(tBu)_3/B(C_6F_5)_3$,[9] we were also able to locate a transition state associated with the H–H bond cleavage (Figure 6), which is higher in energy by only $\Delta E = +1.1$ kcal mol$^{-1}$ relative to the adduct $\mathbf{B} + H_2$ (Figure 4). In **B**, the carbene and the borane are ideally preorganized for a synergistic interaction with an incoming dihydrogen molecule, and the calculated B–C distances in **B** (4.51 Å) and in the transition structure (4.46 Å) are very similar. With C-H-H and B-H-H angles of 174° and 143°, the H–H bond is not fully aligned with the C–B axis, and the H–H distance of 0.79 Å indicates the presence of an early transition state with regard to H–H bond cleavage. Full cleavage of this bond and formation of the imidazolium borate **3** is predicted to be highly exothermic ($\Delta E = -60.7$ kcal mol$^{-1}$ relative to the free educts **1**, $B(C_6F_5)_3$, and $H_2$; Figure 6). In comparison with the energy calculated for the formation of $[(tBu)_3PH][HB(C_6F_5)_3]$ from $P(tBu)_3$, $B(C_6F_5)_3$, and $H_2$ ($\Delta E = -26.3$ kcal mol$^{-1}$),[9] it is obvious

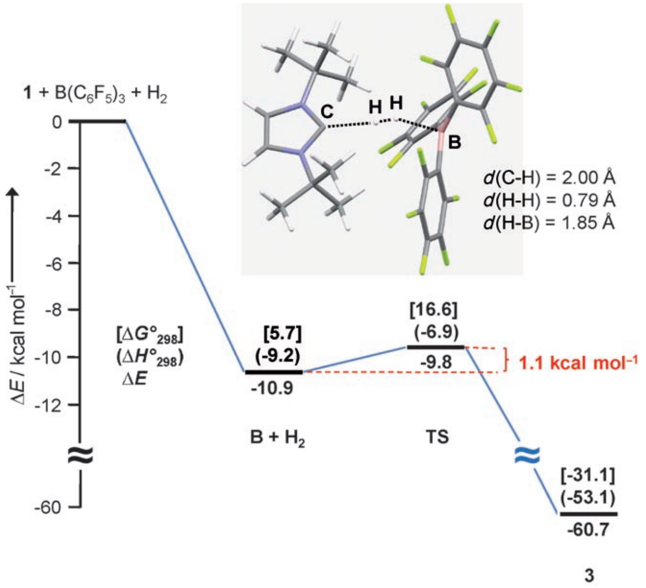

***Figure 6.*** Structure of the transition state and potential-energy profile for heterolytic dihydrogen cleavage with **1**/B(C$_6$F$_5$)$_3$. Values correspond to $\Delta E$ = zero-point uncorrected M05-2X/6-311G(d,p) electronic energies, $\Delta H°_{298}$ = enthalpies at 298 K (in round brackets), and $\Delta G°_{298}$ = Gibbs free energies at 298 K [in square brackets]. TS = transition state.

that heterolytic dihydrogen cleavage is thermodynamically significantly more favorable for carbene–borane systems. However, the strongly exothermic and exergonic nature of this process is likely to prevent the use of these systems for reversible dihydrogen activation.

The present experimental and theoretical study of heterolytic dihydrogen activation by a frustrated carbene–borane Lewis pair reveals that Lewis basic N-heterocyclic carbenes in combination with Lewis acidic boranes have great potential for the activation of small molecules and enthalpically strong bonds, such as C–O, H–H and C–H bonds. The ability to cleave C–H bonds became apparent by the observation that the 1,3-di-*tert*-butylimidazolin-2-ylidene (**1**) used in this study is activated at the 4-position, converting the frustrated normal carbene adduct into a non-frustrated abnormal adduct with concomitant loss of reactivity towards dihydrogen. Further development of these systems should involve N-heterocyclic carbenes that do not provide reactive C–H bonds, which could presumably be achieved by blocking the 4,5-positions, e.g. through dialkylation[13,18] or benzanellation.[19]

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[20] Details of the electronic structure calculations and of the X-ray crystal structure determinations can be found in the Supporting Information. CCDC-690590 (**2**), CCDC-690591 (**3**), and CCDC-690592 (**4**·$CHCl_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.