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Addition of dihydrogen to a borylborenium center†

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The activation of a H–H bond, the simplest covalent bond, is a fundamentally important process. Addition of H₂ to an elemental center typically occurs on low valent transition metal or main group complexes through oxidative addition to afford metal dihydride complexes. In contrast, activation of H₂ on a high valent center generally results in heterolytic cleavage of the H–H bond to a proton and hydride. Here, we report experimental and computational evidence for the addition of H₂ to a borenium center in an N-heterocyclic carbene (NHC) coordinated borylborenium cation, which leads to the formation of a dihydroborenium complex accompanied by the elimination of two σ -bonded substituents, namely mesityl (Mes) and pinacolboryl (Bpin) groups, as mesitylborynic ester.

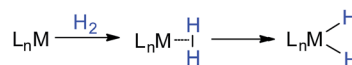
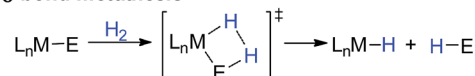
Introduction

The activation of dihydrogen is a key step for hydrogenation reactions, which are considered as “the largest-volume human-made chemical reactions in the world”.^{1,2} In the activation process, the H–H σ bonding orbital is depopulated along with population of the H–H σ^* anti-bonding orbital. Possessing empty/filled d orbitals suitable for interaction with H₂ orbitals, low valent transition metal complexes can activate H–H bonds through oxidative addition, affording metal-dihydride complexes (Scheme 1a).¹ Such oxidative addition is not limited to transition metal complexes. Low valent main group complexes, such as carbenes,³ silylenes⁴ and Al(i)⁵ complexes, can also activate H₂ through oxidative addition due to the presence of an empty p orbital and a lone pair on the central element which can synergistically interact with H₂ orbitals. On the other hand, high valent transition metal or main group complexes cannot undergo oxidative addition when treated with H₂ due to their lack of filled d orbitals or lone pairs. Instead, they can activate H₂ through either σ bond metathesis or base-assisted activation (Scheme 1b and c). The former pathway mainly involves d⁰ or d⁰fⁿ metal complexes, resulting in hydrogenolysis of one M–E σ bond and the formation of a hydride species and H–E compound.⁶ The latter pathway includes synergistic interaction of a Lewis acid and base with H₂, exemplified by the well-studied Noyori catalysts⁷ and the recently emerging frustrated Lewis pairs (FLPs),⁸ which leads to the formation of a hydride species and a protonated base. In contrast, the addition of H₂ to a high valent element center to

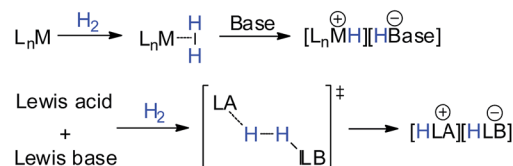
afford dihydride species still remains unknown (Scheme 1d).⁹ Such a reaction pathway would involve the cleavage of three σ -bonds with the concomitant formation of three new ones.

Recently, we¹⁰ and the group of Nikonov¹¹ independently discovered that electrophilic hydroboranes can activate H₂ in the absence of Lewis bases through σ bond metathesis at 60 °C. Miqueu, Bouhadir and Bourissou *et al.* reported that phosphine coordinated mesitylborenium complexes can react with H₂ at 80 °C to afford corresponding hydroborenium complexes and mesitylene.^{12,13} Our theoretical investigation suggests that the charge transfer from the bonding orbital of a B–E bond to the σ^* anti-bonding orbital of H₂ plays an important role in the H₂ activation process.¹⁴ To increase the reactivity of organoboranes

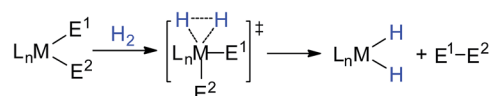
a) oxidative addition

b) σ bond metathesis

c) base assisted activation



d) concurrent addition/elimination (this work)

Scheme 1 Mechanisms for the activation of H₂.

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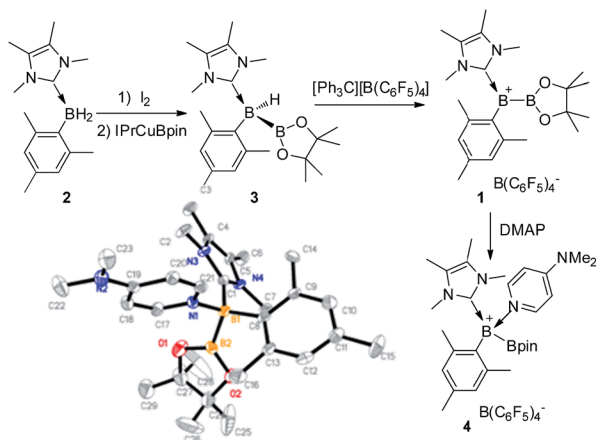


against H_2 , we synthesized an N-heterocyclic carbene (NHC) coordinated borylborenium cation (**1**),^{15,16} anticipating that the boryl substituent would enhance the interaction between the B–B bonding orbital and the σ^* anti-bonding orbital of H_2 . Indeed, borenium **1** was found to be able to activate H_2 at a temperature as low as -40°C . Additionally, to our surprise, the borenium center was inserted into the H–H bond, affording a dihydroborenium complex. Herein we report the synthesis of borenium **1** and its reactivity against H_2 along with experimental and theoretical investigation of the reaction mechanism.

Results and discussion

Synthesis of **1** and its reactivity against H_2

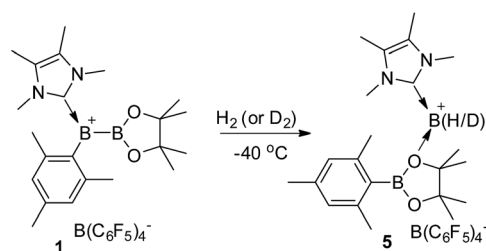
To prepare the precursor for borenium **1**, Ime_4 borane derivative $\text{Ime}_4\text{B}(\text{H})_2\text{Mes}$ (**2**, Ime_4 = 1,3,4,5-tetramethylimidazol-2-ylidene) was treated with I_2 ¹⁷ to afford $\text{Ime}_4\text{B}(\text{H})(\text{I})\text{Mes}$, which was not isolated but directly reacted with IPrCuBpin (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, Bpin = pinacolboryl),¹⁸ producing the unsymmetrical diboron complex **3** in 52% yield (Scheme 2). The ^{11}B NMR spectrum of **3** features one singlet at 40.9 ppm and one doublet at -29.5 ppm with the former assigned to the Bpin unit and the latter to the NHC coordinated BH moiety. Hydride abstraction from **3** with one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene at 25°C resulted in near quantitative formation of the borylborenium complex **1**. After purification, complex **1** could be isolated in 96% yield and was characterized using NMR spectroscopy, high resolution mass spectrometry (HRMS) and elemental analysis. In the ^{11}B NMR spectrum of **1**, the resonance corresponding to the NHC coordinated boron atom appears at 78.0 ppm as a broad singlet, which is consistent with the formation of a borenium cation.¹⁵ An upfield shift of the Bpin moiety (32.8 ppm) compared to **3** was also observed. The identity of **1** was further confirmed using derivatization. Treatment of **1** with one equivalent of 4-dimethylaminopyridine (DMAP) gave DMAP coordinated boronium complex **4**, which was characterized using X-ray diffraction.



Scheme 2 Synthesis of **1** and **4**, and the molecular structure of **4** (the hydrogen atoms and counter anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are omitted for clarity).

When the amount of DMAP was increased to two equivalents, complex **4** was still the only observable product and no bis-DMAP adduct was produced.

When treated with 1.5 bar H_2 in a toluene solution at room temperature, borenium **1** was quantitatively converted to a new species **5** in less than one minute. This reaction can take place at a much lower temperature. Stirring of the solution of **1** under 4.0 bar H_2 for 2 hours at -40°C also resulted in the quantitative formation of **5** (Scheme 3). This represents the mildest conditions for the activation of H_2 by an organoboron species.^{19,20} Although complex **5** decomposes to unidentified complexes in bromobenzene solution after 1 day at room temperature, it was fully characterized using NMR and HRMS analysis. In the ^1H NMR spectrum of **5**, a broad signal at δ 2.87 ppm was observed, which was assigned to a BH_2 moiety after comparison with the corresponding $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum. We also noticed that the signal for the pinacol moiety appears as a broad singlet at δ 1.26 ppm, which prompted us to carry out a VT-NMR study (Fig. 1). At 60°C , the signal for the pinacol moiety appears as a sharp singlet at δ 1.30 ppm. Upon cooling to -20°C , this signal decoalesces to two broad singlets (δ 1.39 and 1.12 ppm), implying the existence of inequivalent methyl groups in the pinacol moiety. The signals corresponding to the Mes moiety also become broad during the cooling process, and those for Ime_4 are largely temperature-invariant. In the ^{11}B NMR spectrum of **5** at 25°C , besides the signal from the anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ at δ -15.9 ppm, two broad singlets at δ 33.3 and -7.6 ppm were observed. As the former is in the range of a tricoordinate boron and the latter indicates the formation of a tetracoordinate boron, we assigned compound **5** as the adduct of $[\text{Ime}_4\text{BH}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and MesBpin with the oxygen atom of the pinacol moiety coordinating to the boron center of $[\text{Ime}_4\text{BH}_2]^+$. A similar coordinate mode was observed in a $\text{Bi}(\text{III})$ complex in which the $\text{Bi}(\text{III})$ center is coordinated by the oxygen atom of a borate ester moiety.²¹ In agreement with this assignment, HRMS analysis of **5** revealed the formation of fragments $[\text{Ime}_4\text{BH}_2]^+$ and $[\text{MesBpinLi}]^+$ (Li ion was added as an ionization source). Our assignment was further confirmed by the independent synthesis of compound **5** from the borenium salt $[\text{Ime}_4\text{BH}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ²² and MesBpin, which shows identical NMR spectra. The MesBpin moiety in **5** is readily replaced by a stronger base such as DMAP, affording the literature known boronium salt $[\text{Ime}_4\text{B}(\text{H})_2(\text{DMAP})][\text{B}(\text{C}_6\text{F}_5)_4]$ ²² and free MesBpin. Treatment of **1** with D_2 resulted in the formation of the corresponding deuterated analog **5-D}_2. The ^2H NMR spectrum**



Scheme 3 Reaction of borylborenium **1** with H_2 or D_2 .



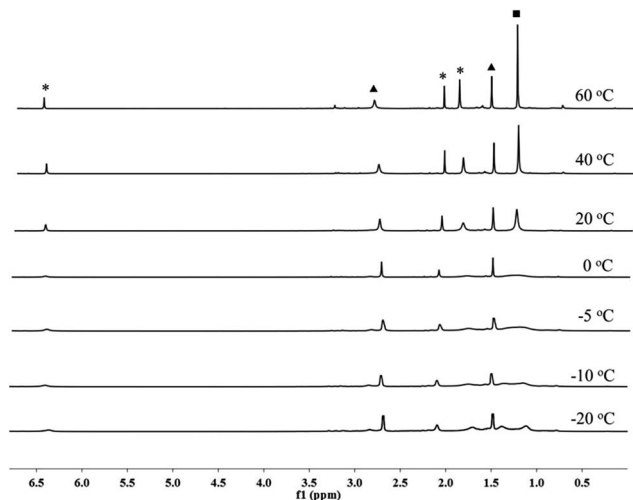


Fig. 1 VT-NMR spectra of **5** in C_6D_5Br (■: Bpin, ▲: IMe_4 , *: Mes).

of **5-D₂** displays a broad resonance at δ 2.86 ppm originating from the BD_2 moiety.²³ After quenching with DMAP, $[IMe_4-B(D)_2(DMAP)][B(C_6F_5)_4]$ and MesBpin were obtained, confirming that the two hydride substituents in **5** originate from H_2 . To the best of our knowledge, this is the first time that the insertion of a boron center to a H–H bond has been observed.²⁴ In a related study, Stephan and Bertrand reported that an acyclic(alkyl)(amino)carbene supported borylene can undergo a 1,2-addition reaction when treated with H_2 and a dihydroboron species was proposed as a transient intermediate from the oxidative addition of H_2 on the boron center.²⁵ Recently, the groups of Wagner²⁶ and Yamashita²⁷ discovered that diboron species, such as reduced 9,10-dihydro-9,10-diboranthracene and (*o*-Tol)₂BB(*o*-Tol)₂, can function as FLPs to react with H_2 , affording hydroborane complexes.

Experimental mechanism studies

To probe the reaction mechanism, we carried out a kinetic study of the reaction between **1** and H_2 which was monitored using 1H NMR spectroscopy. Besides the starting material **1**, H_2 and the final product **5**, no intermediate was observed in the reaction mixture. The rate of disappearance of **1** under a 10-fold excess of H_2 followed pseudo-first-order kinetics. A linear dependence of the observed rate constant k_{obs} on the H_2 pressure at $-15^\circ C$ suggested a first-order dependence on H_2 pressure. These data were consistent with an overall second-order rate law for the H_2 activation reaction. Kinetic measurements at temperatures ranging from -45 to $-5^\circ C$ allow the determination of activation parameters ($\Delta H^\ddagger = 6.2(2) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -33.8(6) \text{ cal mol}^{-1} \text{ K}^{-1}$) (Fig. 2a). The low value of ΔS^\ddagger implies an associative mechanism. Furthermore, an inverse kinetic isotope effect ($KIE = 0.80$) was obtained by measuring the rate constant of the reaction between **1** and D_2 (Fig. 2b), which indicates the existence of a dihydrogen complex in a rapid equilibrium before the H–H bond is cleaved.¹ Observations of inverse KIEs for H_2 activation reactions are rare. We only noticed two examples in the literature, which involve Ir^{28} and Fe^{29} complexes.

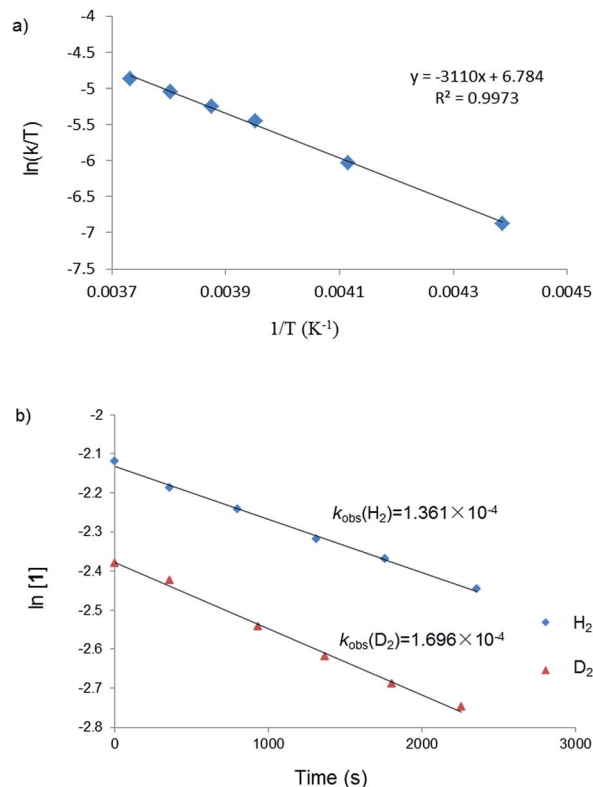
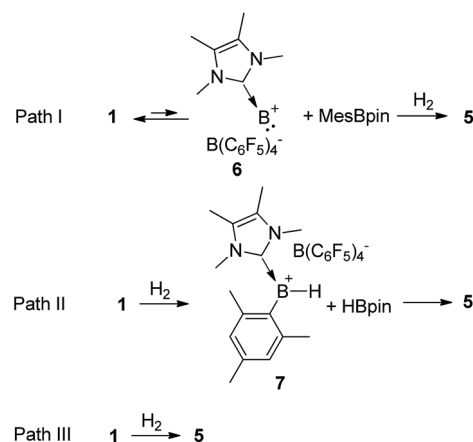


Fig. 2 (a) Eyring plot of the reaction between **1** and H_2 ; (b) plots of the reactions between **1** and H_2 or D_2 at 258 K.

Based on the kinetic study, three possible mechanisms could be considered for the formation of complex **5** from borenium **1** and H_2 . One mechanism (Scheme 4, path I) is that borenium **1** undergoes reductive elimination to afford borinylium intermediate **6**, followed by the oxidative addition of H_2 and coordination of MesBpin to form complex **5**. The second proposed mechanism (Scheme 4, path II) involves the initial formation of $[IMe_4B(H)Mes][B(C_6F_5)_4]$ (**7**) and HBpin,²⁶ which subsequently go through ligand exchange to form complex **5**. A third mechanism (Scheme 4, path III) would be that the addition of H_2 and



Scheme 4 Possible reaction pathways for the formation of complex **5**.



elimination of MesBpin occur in a concomitant manner. Both of the latter two pathways could proceed *via* initial coordination of H₂ to the borenium center of **1**.

If path I is operative, the reductive elimination and the reverse reaction, oxidative addition, must be very facile. To test this hypothesis, we mixed equimolar amounts of borenium **1** and (Mes-*d*₉)(Bpin-*d*₁₂) in toluene and no H/D scrambling was observed even at 80 °C. Therefore, path I can be ruled out. To test the feasibility of path II, we synthesized borenium **7** and studied its reactivity against HBpin. Mixing equimolar amounts of **7** and HBpin at room temperature led to the quantitative formation of **5** in one minute. When this reaction took place at −78 °C, complete conversion to **5** was observed after 10 min. No adduct of **7** and HBpin was observed while monitoring this reaction at −78 °C using ¹¹B NMR spectroscopy (Fig. S45†). Subsequent kinetic study revealed that the activation parameters Δ*H*[‡] and Δ*S*[‡] for this reaction are 2.5(1) kcal mol^{−1} and −44.9(3) cal mol^{−1} K^{−1}, respectively.

To distinguish paths II and III, we examined the reaction of an equimolar mixture of **1** and the deuterated analog [IMe₄-B(Bpin-*d*₁₂)(Mes-*d*₉)] [B(C₆F₅)₄] (**1-D**) with H₂ in toluene (no H/D scrambling was observed for this mixture before H₂ was introduced). If path II is effective, one would anticipate the observation of the non-crossover products (MesBpin and (Mes-*d*₉)(Bpin-*d*₁₂)) and crossover products (Mes(Bpin-*d*₁₂) and (Mes-*d*₉)Bpin) in a 1 : 1 ratio after quenching with DMAP, as the solvent cage effect should only play an insignificant role in the second step in path II due to the comparatively high free-energy barrier of this step. Alternatively, path III would lead to the observation of only the non-crossover products, as the H/D scrambling of complex **5** and its deuterium analog [IMe₄-B(H)₂(Mes-*d*₉)(Bpin-*d*₁₂)] [B(C₆F₅)₄] was found to be much slower (less than 1% crossover product was observed after stirring for 30 min at room temperature).

Intriguingly, the observed ratios of non-crossover to crossover products imply that this reaction could proceed through both paths II and III with the latter favored at lower temperature (Table 1). When this reaction is conducted at −78 °C, the ratio of non-crossover to crossover products is 90 : 10.

Increasing the reaction temperature to 10 °C resulted in a decrease in the ratio to 73 : 27. Using the ratio of non-crossover to crossover products, we can estimate the ratio of the rate constants for path II and III, *k*_{II}/*k*_{III} (for calculation details see ESI†), and thus approximate ΔΔ*H*[‡] and ΔΔ*S*[‡], which are

Table 1 The ratio of rate constants for path II and path III (*k*_{II}/*k*_{III}) at various temperatures

Entry	Temp. (K)	Non-crossover : crossover products	<i>k</i> _{II} / <i>k</i> _{III}
1	195	90 : 10	0.24
2	213	87 : 13	0.36
3	233	82 : 18	0.54
4	253	80 : 20	0.69
5	273	76 : 24	0.91
6	283	73 : 27	1.18

estimated to be 1.9(1) kcal mol^{−1} and 6.9(4) cal mol^{−1} K^{−1}, respectively. However, from the experimental data, we cannot tell whether this activation parameter difference corresponds to the rate-determining step (RDS) or a product-determining step after the RDS.

Theoretical studies

To further understand the reaction mechanism, the free-energy profile of this reaction was computed using density functional theory (DFT) calculations (M06-2X) (Fig. 3).³⁰ First, H₂ coordinates to the borenium center (B1) of **1** to form a dihydrogen complex **1**·H₂ through transition state **TS1**, in which the H–H bond is slightly activated and elongated from 0.737 to 0.817 Å. Subsequently, H₂ is cleaved to form an intermediate **IM1** through transition state **TS2**, which is the rate-limiting step. **TS2** is 15.6 kcal mol^{−1} greater than free **1** and H₂ in free energy, which is comparable to the experimental value of 16.3 kcal mol^{−1}. In **TS2**, the H–H bond is substantially weakened and elongated to 1.040 Å. Both H atoms are closely bonded to the B1 atom with B1–H1 and B1–H2 bond distances of 1.269 and 1.244 Å, respectively. Unlike the four-centered transition state for σ bond metathesis,⁶ only a very weak interaction between B2 and the H2 atom (1.729 Å) is observed, which corresponds to a bond order of 0.11 according to natural bond orbital (NBO) analysis. The B1–B2 bond in **TS2** is significantly weakened as well, and its distance is increased from 1.708 Å in **1** to 1.761 Å. In **IM1**, the H–H bond is completely cleaved. Concomitantly, a B1–H1 bond is observed with a bond length of 1.192 Å. The H2 atom forms a highly unsymmetrical three-center two-electron (3c2e) bond with B1 and B2, and the B1–H2 and B2–H2 bond distances are 1.245 and 1.469 Å, respectively. Interestingly, the *ipso* carbon atom of the mesityl moiety also forms a B–C–B 3c2e bond with B1 and B2, and the B1–C1 and B2–C1 bond distances are 1.708 and 1.765 Å, respectively. As a result, **IM1** can be considered as an adduct of borenium [IMe₄BH₂]⁺ and MesBpin linked with two 3c2e bonds.³¹ **IM1** can

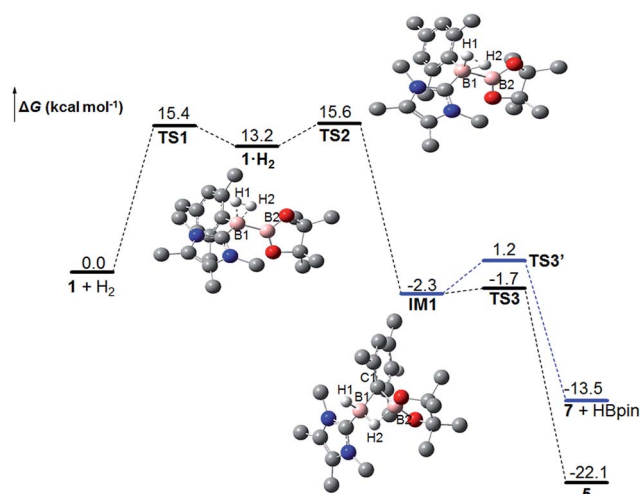


Fig. 3 The Gibbs free energy profile at 298 K for the reaction between **1** and H₂ (H atoms (except H1 and H2) are omitted for clarity).



rearrange to the final product **5** through transition state **TS3** with a very low free-energy barrier of 0.5 kcal mol⁻¹, which can be deemed as following path III in Scheme 4. On the other hand, **IM1** can also undergo a reversible ligand exchange through **TS3'** to afford **7** and HBpin, which are 8.6 kcal mol⁻¹ less stable than **5** in free energy. The reaction from **7** and HBpin to **5** through **IM1** needs to overcome a free-energy barrier of 14.7 kcal mol⁻¹, which is in good agreement with our experimental value (15.9 kcal mol⁻¹). This pathway corresponds to path II in Scheme 4. Therefore, these calculation results clearly show that the observation of the crossover experiment is not due to the existence of two H₂ activation pathways. Instead, the observed crossover products originate from the ligand exchange of **IM1** following the cleavage of the H-H bond, and the percentage of crossover product in the crossover experiment is determined by the free-energy difference between **TS3** and **TS3'**. The calculated $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values between **TS3'** and **TS3** are 4.7 kcal mol⁻¹ and 5.6 cal mol⁻¹ K⁻¹, respectively, and are in relatively good agreement with the experimental values. We also calculated the KIE value for this reaction and the computed value of 0.81 agrees very well with the measured KIE value.

To obtain insight into the H-H bond activation process, NBO population analysis along the intrinsic reaction coordinate (IRC) was carried out. As shown in Fig. 4, the electron populations³² of both hydrogen atoms are quite similar throughout the whole process, clearly indicating that the H-H bond is cleaved in a homolytic manner. During the process of coordination of H₂ to **1** to form **1·H₂**, the electron populations of the H1 and H2 atoms decrease by 0.26 and 0.28 e, respectively. NBO occupation analysis revealed that these population changes are mainly due to the charge transfer from the H-H σ bond orbital to the empty p orbital of the B1 atom; the loss of the occupancy of the H-H σ bond orbital (0.60 e) matches very well with the increase of the occupancy of the p orbital of the B1 atom (0.62 e). This charge transfer results in an increase of the population of the B1 atom by 0.75 e, which induces polarization of the B-B σ bond towards the B1 atom and a decrease of the population of the B2 atom by 0.16 e. The contribution from the

atomic orbitals of B1 to the B-B σ bonding orbital also increases from 52% in **1** to 59% in **1·H₂**. Such polarization is even larger than a known boryltitanium complex in which the boron atom contributes 54% of the Ti-B bond.³³ This polarization of the B-B bond is in sharp contrast with the well-studied Lewis base coordinated B₂pin₂ complexes in which the B-B bond is polarized to the sp² boron atom.^{33b,34} The IMe₄ and mesityl ligands of the B1 atom in **1** are likely responsible for this counter-intuitive observation. Unlike the pinacol ligand, which can be an efficient electron-withdrawing group at an sp³ hybridized B atom,^{33b,34b} neither IMe₄ nor Mes can effectively draw electron density from the B1 atom when it receives electron charge from H₂.

As the reaction proceeds from **1·H₂** to **TS2**, the H-H σ^* orbital gains 0.20 e, accompanied with a loss of 0.17 e from the B-B σ orbital, which is consistent with a charge transfer from the B-B σ orbital to the H-H σ^* orbital. Due to the polarization of the B-B σ bond (the contribution from the atomic orbitals of B1 is 60%), this charge transfer predominately originates from the B1 atom. The back donation from the B1 atom, combined with the concomitant charge transfer from the H-H σ bond orbital to the empty p orbital of the B1 atom, ensures that both H atoms strongly coordinate to the B1 atom (the bond orders of B1-H1 and B1-H2 are 0.64 and 0.54 respectively). Furthermore, the polarization of the B-B bond results in an increase of positive charge on the Bpin moiety in **TS2** ($q = 0.21$) compared to **1** ($q = 0.04$), which induces the migration of the electron-rich mesityl group from the B1 to B2 atom to form a B-C-B 3c2e bond in **IM1**.

Conclusions

In this work we have reported the synthesis of an NHC-coordinated borylborenium complex (**1**). When this borylborenium complex was treated with H₂, addition of H₂ to the borenium center was observed along with elimination of mesityl and Bpin substituents. The mechanistic studies revealed an unprecedented concurrent addition/elimination process in which polarization of the B-B bond upon coordination of H₂ plays a critical role. Our discovery advances the understanding of dihydrogen activation involving high valent species, and may offer a new pathway for the activation of a broader range of element-element bonds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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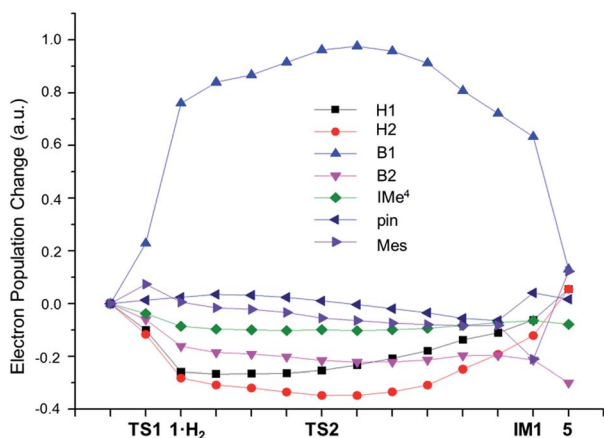


Fig. 4 Electron population change along the IRC of the reaction between **1** and H₂.



Notes and references

- G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152–4205.
- J. G. de Vries and C. J. Elsevier, *The Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, 2007.
- G. D. Frey, V. Lavallo, B. Donnadiou, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439–441.
- A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503.
- T. Chu, I. Korobkov and G. I. Nikonov, *J. Am. Chem. Soc.*, 2014, **136**, 9195–9202.
- R. Waterman, *Organometallics*, 2013, **32**, 7249–7263.
- R. Noyori and T. Ohkuma, *Angew. Chem., Int. Ed.*, 2001, **40**, 40–73.
- (a) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126; (b) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76; (c) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441; (d) D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032.
- Addition of covalent bonded species, such as Cl₂, to high valent metal complexes with non-innocent supporting ligands is known, see: K. J. Blackmore, J. W. Ziller and A. F. Heyduk, *Inorg. Chem.*, 2005, **44**, 5559–5561.
- Z. Lu, Z. Cheng, Z. Chen, L. Weng, Z. H. Li and H. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 12227–12231.
- G. I. Nikonov, S. F. Vyboishchikov and O. G. Shirobokov, *J. Am. Chem. Soc.*, 2012, **134**, 5488–5491.
- (a) M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **54**, 5722–5726; (b) M. Devillard, S. Mallet-Ladeira, G. Bouhadir and D. Bourissou, *Chem. Commun.*, 2016, **52**, 8877–8880.
- For examples of the activation of H₂ with borenium complexes in the presence of bases, see: (a) J. M. Farrell, J. A. Hatnean and D. W. Stephan, *J. Am. Chem. Soc.*, 2012, **134**, 15728–15731; (b) E. R. Clark, A. Del Grosso and M. J. Ingleson, *Chem.–Eur. J.*, 2013, **19**, 2462–2466; (c) P. Eisenberger, B. P. Bestvater, E. C. Keske and C. M. Crudden, *Angew. Chem., Int. Ed.*, 2015, **54**, 2467–2471.
- Y. Wang, W. Chen, Z. Lu, Z. H. Li and H. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 7496–7499.
- D. P. Curran, A. Solov'ev, M. M. Brahmi, L. Fensterbank, M. Malacria and E. Lacôte, *Angew. Chem., Int. Ed.*, 2011, **50**, 10294–10317.
- For examples of borylboreniums see: (a) H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kramer, T. Kupfer, K. Radacki, E. Siedler, A. Trumpp, K. Wagner and C. Werner, *J. Am. Chem. Soc.*, 2013, **135**, 8702–8707; (b) A. Prokof'evs, *Angew. Chem., Int. Ed.*, 2015, **54**, 13401–13405.
- A. Solov'ev, Q. Chu, S. J. Geib, L. Fensterbank, M. Malacria, E. Lacôte and D. P. Curran, *J. Am. Chem. Soc.*, 2010, **132**, 15072–15080.
- D. S. Laitat, P. Müller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196–17197.
- (a) C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 9604–9606; (b) A. Y. Houghton, V. A. Karttunen, C. Fan, W. E. Piers and H. M. Tuononen, *J. Am. Chem. Soc.*, 2013, **135**, 941–947.
- In the presence of Lewis bases, organoboranes are known to activate H₂ even at –78 °C, for examples see (a) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7428–7432; (b) P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433–7437; (c) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan and J. Paradies, *Angew. Chem., Int. Ed.*, 2012, **51**, 10164–10168.
- C. C. Caries and S. Guccione, *Organometallics*, 2008, **27**, 747–752.
- A. Prokof'evs, J. W. Kampf, A. Solov'ev, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2013, **135**, 15686–15689.
- Observation of no H/D scrambling in Mes group eliminates the potential mechanism involving hydrogenolysis of B–C bond and subsequent C–H borylation.
- For examples of heterolytic cleavage of H₂ along B–E bonds see ref. 19 and S. J. Geier, T. M. Gilbert and D. W. Stephan, *J. Am. Chem. Soc.*, 2008, **130**, 12632–12633.
- F. Dahcheh, D. Martin, D. W. Stephan and G. Bertrand, *Angew. Chem., Int. Ed.*, 2014, **53**, 13159–13163.
- E. v. Grotthuss, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2016, **55**, 14067–14071.
- N. Tsukahara, H. Asakawa, K.-H. Lee, Z. Lin and M. Yamashita, *J. Am. Chem. Soc.*, 2017, **139**, 2593–2596.
- B. E. Hauger, D. Gusev and K. G. Caulton, *J. Am. Chem. Soc.*, 1994, **116**, 208–214.
- J. M. Camara and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2011, **133**, 8098–8101.
- (a) Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101–194118; (b) Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 5121–5129.
- A. Hübner, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2012, **51**, 12514–12518.
- Electron population of an atom is the total number of electrons on the atom. A positive value represents an increase of population relative to that of 1 and H₂.
- (a) T. Terabayashi, T. Kajiwar, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14162–14163; (b) J. Cid, J. J. Carbó and E. Fernández, *Chem.–Eur. J.*, 2012, **18**, 12794–12802.
- (a) K.-s. Lee, A. R. Zhugralin and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 7253–7255; (b) A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás and E. Fernández, *Angew. Chem., Int. Ed.*, 2011, **50**, 7158–7161.

