

The Hydride-Ion Affinity of Borenium Cations and Their Propensity to Activate H₂ in Frustrated Lewis Pairs

Ewan R. Clark, Alessandro Del Grosso, and Michael J. Ingleson*^[a]

Abstract: A range of frustrated Lewis pairs (FLPs) containing borenium cations have been synthesised. The catechol (Cat)-ligated borenium cation [CatB(PrBu₃)]⁺ has a lower hydride-ion affinity (HIA) than B(C₆F₅)₃. This resulted in H₂ activation being energetically unfavourable in a FLP with the strong base PrBu₃. However, ligand disproportionation of CatBH(PrBu₃) at 100 °C enabled trapping of H₂ activation products. DFT calculations at the M06-2X/6-311G(d,p)/PCM (CH₂Cl₂) level revealed that replacing catechol

with chlorides significantly increases the chloride-ion affinity (CIA) and HIA. Dichloro-borenium cations, [Cl₂B(amine)]⁺, were calculated to have considerably greater HIA than B(C₆F₅)₃. Control reactions confirmed that the HIA calculations can be used to successfully predict hydride-transfer reactivity between borenium cations

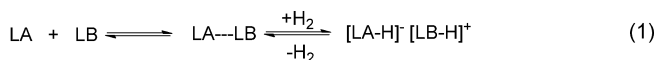
and neutral boranes. The borenium cations [Y(Cl)B(2,6-lutidine)]⁺ (Y = Cl or Ph) form FLPs with P(mesityl)₃ that undergo slow deprotonation of an *ortho*-methyl of lutidine at 20 °C to form the four-membered boracycles [(CH₂[NC₅H₃Me])B(Cl)Y] and [HPMes₃]⁺. When equimolar [Y(Cl)B(2,6-lutidine)]⁺/P(mesityl)₃ was heated under H₂ (4 atm), heterolytic cleavage of dihydrogen was competitive with boracycle formation.

Keywords: borenium cations • boron • density functional calculations • frustrated Lewis pairs • hydrides

Introduction

Sterically frustrated Lewis pairs (FLPs) utilise unquenched Lewis acidity and basicity for the concerted activation of small molecules.^[1,2] This field has developed rapidly since Stephan's breakthrough publication in 2006,^[3] with a range of impressive transformations reported including the reversible activation of H₂ and the catalytic reduction of unsaturated and aromatic moieties.^[4–16] A plethora of Lewis bases, ranging from moderately basic (2,4,6-trimethylphenyl)₃P (PMes₃) to strongly basic N-heterocyclic carbenes (NHCs), have been successfully employed in FLP H₂ activation. In contrast, excluding a limited number of notable exceptions,^[17–20] the Lewis acidic component has largely been limited to highly fluorinated aryl boranes, particularly B(C₆F₅)₃. This is due to a minimum cumulative Lewis acid (LA)/base (LB) strength being a prerequisite for H₂ activation by a FLP.^[9,21,22] Studies using FLPs containing alternative boranes have shown that even a modest reduction in borane Lewis acidity, relative to B(C₆F₅)₃, can shift the H₂ activation equi-

librium [Eq. (1)] drastically towards the neutral starting materials, even when using a strong LB.^[23–25]



Borenium cations are three coordinate borocations^[26] that can possess considerable Lewis acidity engendered by the positive charge.^[27] Recently, this high electrophilicity has been utilised for applications in organic transformations.^[28,29] We have previously synthesized borocation-based FLPs based on catechol and thiocatechol (*o*-C₆H₄S₂) ligated borenium cations,^[30] and are interested in using these and other borenium cations in FLPs for H₂ activation. Borenium cations can be more electrophilic than B(C₆F₅)₃, and high Lewis acidity towards hydride ions should enable the extension of FLP activation of H₂ towards weaker LBs. Recognizing the potential of highly electrophilic cationic LAs in FLPs, Müller et al. have recently reported that a silicenium cation [(Me₅C₆)₃Si]⁺ formed an FLP with PMes₃ that rapidly cleaved H₂. However, this FLP did not activate H₂ with weakly basic P(C₆F₅)₃.^[17] Borenium cations are valence isoelectronic to silicenium cations, and a first indication that they could activate H₂ came from the work of Vedejs et al., who observed deuterium incorporation on heating **1** under a D₂ atmosphere (Figure 1, top).^[31] Although the heterogeneous nature of this system precluded mechanistic elucidation, H₂ activation by a FLP was one possibility. Insight into the hydride-ion affinity (HIA) of borenium cations, particularly relative to B(C₆F₅)₃, is limited. One exception comes from the work of Stephan et al., which synthesized [CatB-

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Supporting information for this article contains experimental details, full crystal structure determination data, additional NMR spectroscopic discussion and explicit spectra, as well as details of the quantum chemical calculations including total energies and xyz coordinates. It is available on the WWW under <http://dx.doi.org/10.1002/chem.201203318>.

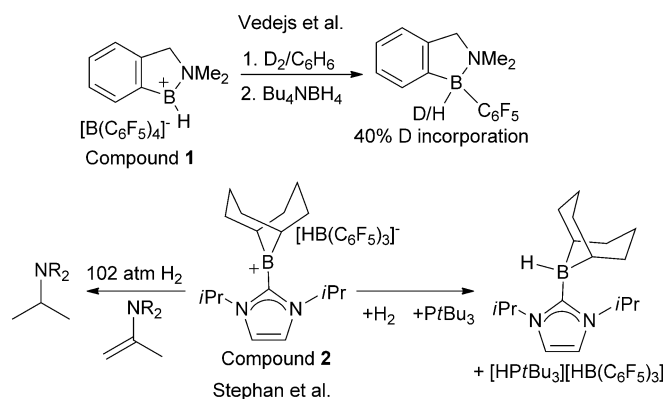


Figure 1. Recent examples of H_2 activation by borocations and the application of **2** as a catalyst for the hydrogenation of enamines.

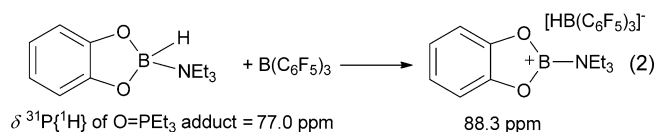
$(PtBu_3)[HB(C_6F_5)_3]$ by hydride-ion transfer from $CatBH(PtBu_3)$ to $B(C_6F_5)_3$.^[32] More recently, the same group reported the first definitive FLP-based activation of H_2 by using a borenium cation **2** (Figure 1, bottom). Compound **2** also has a lower HIA than $B(C_6F_5)_3$ based on hydride-transfer reactivity.^[33] Borenium cations are particularly attractive for catalysis, because they are inexpensive and simple to produce whilst being easily modified to vary electrophilicity and steric factors. Their catalytic utility has been recently demonstrated by Stephan et al. with **2** proving a highly effective hydrogenation catalyst that combines high activity with improved selectivity and functional-group tolerance compared to $B(C_6F_5)_3$ and its derivatives.^[33]

Herein, we report our recent studies into the incorporation of borenium cations into FLPs for H_2 activation. This includes combined experimental and computational studies demonstrating that borocations possess an extremely wide range (>30 kcal mol⁻¹) of HIAs. Significantly, dichloro-ligated borenium cations were found to have considerably greater HIA than that of $B(C_6F_5)_3$. A number of FLPs constructed from phosphine- and amine-ligated borenium cations are accessible including examples that activate H_2 .

Results and Discussion

FLPs containing catecholato-ligated borenium cations: $[CatB(amine)]^+$ cations have HIA lower than that of $B(C_6F_5)_3$ with hydride transfer observed upon addition of $B(C_6F_5)_3$ to $CatBH(amine)$ to form $[CatB(amine)][HB(C_6F_5)_3]$ (amine = Et_3N and 4, *N,N*-trimethylaniline). This is in contrast to the relative Lewis acidities determined by the Gutmann–Beckett method.^[34,35] The greater downfield chemical shift of the phosphorus resonance of Et_3PO upon coordination to $[CatB(NEt_3)]^+$ indicates that this borenium cation is more Lewis acidic towards Et_3PO than $B(C_6F_5)_3$ [Eq. (2)]. Furthermore, we have previously reported that $[CatB(NEt_3)]^+$ abstracts fluoride from $[SbF_6]^-$,^[30] indicating that this borenium cation has an extremely high fluoride-ion

affinity (FIA), which is greater than that of $B(C_6F_5)_3$ (FIA of $SbF_5 = 489$ compared to a FIA of 444 kJ mol⁻¹ for $B(C_6F_5)_3$).^[36] Clearly, there is a distinction between the Lewis acidity of $[CatB(amine)]^+$ towards highly electronegative atoms and towards less electronegative moieties (e.g., hydrides). Presumably this is due to the large electrostatic component to bonding between boron and F^- or Et_3PO^- , consistent with Pearson's classic hard-soft acid-base theory.^[37] Hence, borocations, such as $[CatB(NEt_3)]^+$, which have a high calculated natural bond order (NBO) positive charge at boron (+1.365e at the MPW1K/6-311 + G(d,p) level)^[30] are highly Lewis acidic towards hard bases, but less so towards hydrides. This is related to Britovsek's observation on the reversal of the relative Lewis acidity of the $B(C_6F_5)_{3-x}(OC_6F_5)_x$ ($x = 0-3$) series with respect to Et_3PO and Et_3PS LBs.^[38]



Although catechol-borenium cations are less Lewis acidic towards hydride than $B(C_6F_5)_3$, it remained feasible that they would activate H_2 in a FLP with a strong LB analogous to the borenium cation **2**.^[33] Because stable FLPs obtained by using $[CatB(NEt_3)]^+$ were not accessible,^[39] the 1:1 mixture of $PtBu_3/[CatB(PtBu_3)][AlCl_4]$ (**3**) was investigated. It displayed broad $^{31}P\{^1H\}$ and ^{11}B NMR resonances ($\delta = 34.9$ and 21.5 ppm, respectively) both devoid of B–P coupling indicative of fluxionality involving B–P bond cleavage.^[39] Multinuclear NMR spectroscopy at $-40^\circ C$ revealed the presence of two major species, the borenium cation **3** and free $PtBu_3$.^[39] Thus, compound **3** and $PtBu_3$ exist as a FLP in equilibrium with its Lewis adduct $[CatB(PtBu_3)]^+$. The addition of H_2 (ca. 4 atm) to equimolar **3**/ $PtBu_3$ in $C_6H_4Cl_2$ (+10% C_6D_6) led to no reaction at $25^\circ C$ (18 h). However, heating this solution to $100^\circ C$ for 24 h resulted in the formation of products consistent with H_2 activation (Figure 2). The expected initial products from heterolytic H_2 cleavage by **3**/ $PtBu_3$ are $[HPtBu_3]^+$ and $CatBH(PtBu_3)$, but the latter is in equilibrium with $CatBH$ and $PtBu_3$. This system is further complicated by $CatBH/PtBu_3$ disproportionating rapidly

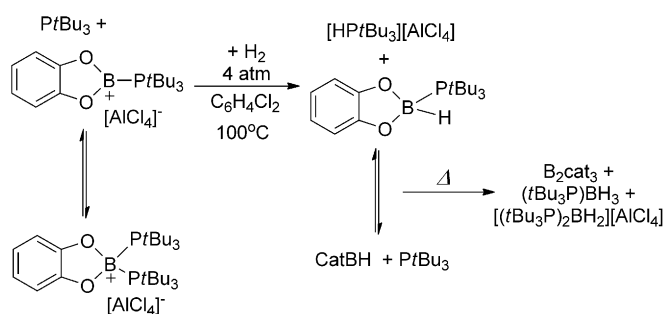
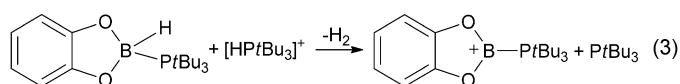


Figure 2. Schematic representation of the equilibrium with **3**/ $PtBu_3$ and activation of H_2 with subsequent ligand disproportionation.

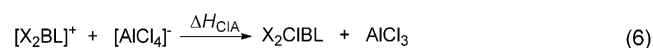
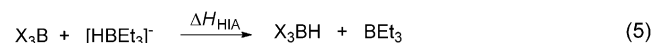
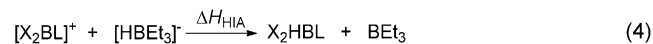
at 100 °C^[40] to form products including B₂cat₃ and (tBu₃P)BH₃ (determined by ¹¹B NMR spectroscopy).^[41,42] Unambiguous confirmation of dihydrogen activation was provided by the exposure of equimolar 3/PtBu₃ to D₂. This led to the formation of [DPtBu₃]⁺ (a 1:1:1 triplet in the ³¹P{¹H} NMR spectrum with P–D coupling of 66 Hz) and broad ¹¹B NMR resonances devoid of B–H coupling.

The requirement for high temperatures before H₂ activation observed with 3/PtBu₃ is attributed to the activation of H₂ being energetically unfavourable due to the lower HIA of [CatB(PtBu₃)]⁺ (relative to B(C₆F₅)₃). A low equilibrium concentration of H₂ activation products is presumably present and the rapid ligand disproportionation of CatBH/PtBu₃ that takes place at 100 °C and drives H₂ activation to completion. This hypothesis is supported by the reverse reaction, that is, the addition of [HPtBu₃][B(C₆H₃Cl₂)₄] to CatBH-(PtBu₃), evolving H₂ at 20 °C [Eq. (3)] ([B(C₆H₃Cl₂)₄][−] is termed [BAr^{Cl}][−] from here on).



Assessment of relative HIAs and chloride-ion affinities (CIAs):

Seeking a borenium cation that possesses a greater HIA than B(C₆F₅)₃, the relative HIA of a range of borenium cations was calculated. On the basis of a benchmarking study, M06-2X/6-311G(d,p) was chosen as an optimal compromise between accuracy and computational time.^[39,43] Relative HIAs were calculated from the isodesmic reactions between [HBET₃][−] and the boron LA [Eq. (4) and (5)] analogous to DuBois's approach.^[44] The addition of a polarisable continuum model (PCM) to approximate solvation was essential to prevent over estimation of borenium-cation HIA due to charge neutralization. An analogous affect has been reported when calculating the fluoride-ion affinities (FIA) of phosphonium cations, which led to >100 kcal mol^{−1} over-estimation of FIA.^[45] CIAs relative to AlCl₃ were also estimated by using an approach based on the transfer of chloride from [AlCl₄][−] to the borenium cation [Eq. (6)].^[46] This value is important for determining accessibility of the borenium cation by halide abstraction.



Although there is a general correlation between CIA and HIA, deviations were observed in a number of cases, and these are attributable to two main phenomena: 1) enhancement of relative CIA (compared to relative HIA) due to the increased magnitude of positive charge localized at boron. For example, [CatBNET₃]⁺ has an enhanced CIA versus the thiocatechol analogue [(*o*-C₆H₄S₂)BNET₃]⁺ consistent with

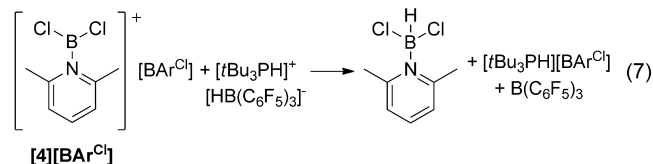
the respective NBO charges at boron of 1.34 and 0.40 e;^[30] 2) the enhanced steric demand of chloride versus hydride. This is particularly noticeable with [Cl₂B(2,6-lutidine)]⁺, ([4]⁺), in which the CIA is significantly lower than expected based on the HIA value. The discrepancy arises from unfavourable steric interactions between the *ortho* methyl groups of lutidine, which are directed towards the boron centre, and one of the three chlorides in (lutidine)BCl₃. Steric crowding in four coordinate (at boron) (*i*Pr–NHC)BH(C₈H₁₄) presumably contributes to the low HIA of cation [2]⁺, which is not stabilised by any π-donor ligands (Table 1).

Table 1. Relative hydride- and chloride-ion affinities.

	HIA [kcal mol ^{−1}]	CIA [kcal mol ^{−1}]
	M06-2X/6-311G(d,p) /PCM(CH ₂ Cl ₂) ΔH	M06-2X/6-311G(d,p) /PCM(CH ₂ Cl ₂) ΔH
neutral boranes		
BET ₃	0.0	–
B(C ₆ F ₅) ₃	−41.0	–
borenium cations		
[CatB–PtBu ₃] ⁺ , [3] ⁺	−33.0	27.1
[CatB–NEt ₃ Pr ₂] ⁺	−37.9	30.2
[2] ⁺	−41.6	–
[CatB–NET ₃] ⁺	−43.6	21.8
[(<i>o</i> -C ₆ H ₄ S ₂)B–NET ₃] ⁺	−45.8	27.7
[PhBCl(2,6-lut)] ⁺ , [6] ⁺	−47.8	26.8
[Cl ₂ B–NEt ₃ Pr ₂] ⁺	−61.0	17.3
[Cl ₂ B(2,6-lut)] ⁺ , [4] ⁺	−61.7	20.7
[Cl ₂ B–NET ₃] ⁺	−65.8	8.3
[Py–BCl ₂] ⁺	−67.8	6.3
AlCl ₃	–	0.0

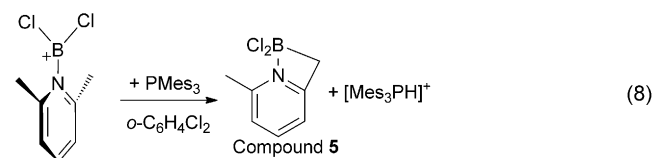
Anion-transfer reactions: To determine if the calculated ΔH values for CIA and HIA allow prediction of solution-phase reactivity, a number of control reactions were investigated. First, all CIAs were positive relative to AlCl₃ consistent with the chloride abstraction experimentally observed on combination of X₂BCl(L) and AlCl₃, forming [X₂BL]–[AlCl₄].^[47,48] The calculated CIAs between borenium cations were also internally consistent, with chloride transfer observed from CatB(NEt₃)Cl to [Cl₂B(2,6-lut)]⁺. Of more importance to this work is the accuracy of the relative HIA of B(C₆F₅)₃ and borenium cations. Cation [4]⁺ has a HIA 20.7 kcal mol^{−1} greater than that of B(C₆F₅)₃; thus [4]⁺ should abstract hydride from [HB(C₆F₅)₃][−]. Pleasingly, mixing [HPtBu₃][HB(C₆F₅)₃][−] and [4][BAr^{Cl}][−] resulted in rapid formation of BCl₂H(2,6-lut), [tBu₃PH][BAr^{Cl}][−] and B(C₆F₅)₃ [Eq. (7)]. This confirms that borenium cations can have higher HIAs than B(C₆F₅)₃. These calculations also correctly predicted the observed abstraction of hydride from CatB(PtBu₃)H by B(C₆F₅)₃. However, [CatB(NEt₃)]⁺ and [2]⁺ were both calculated to have HIAs greater than B(C₆F₅)₃ (by 2.6 and 0.6 kcal mol^{−1}, respectively). Repeating the HIA calculations for BET₃, B(C₆F₅)₃ and [CatB(NEt₃)]⁺ using a basis set including a diffuse function (M06-2X/6-311G+(d,p)/PCM(CH₂Cl₂)) to more accurately model the anionic component resulted in only minor differences. At

this level of theory, the HIA of $\text{B}(\text{C}_6\text{F}_5)_3$ was effectively identical to $[\text{CatB}(\text{NET}_3)]^+$ (44.0 and 44.1 kcal mol $^{-1}$, respectively). Relative HIA calculations are therefore only useful to predict reactivity when there was a considerable difference in ΔH values ($\delta\Delta H$) between the two LAs, as was found for $[\mathbf{4}]^+$ and $\text{B}(\text{C}_6\text{F}_5)_3$.



FLPs containing di-chloride-ligated borenium cations:

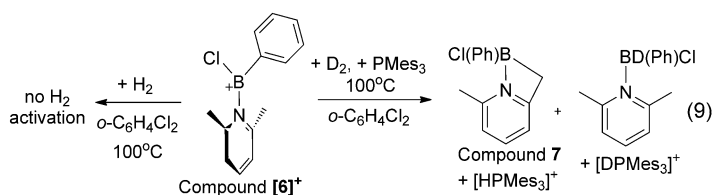
Cation $[\mathbf{4}]^+$ was selected to incorporate into FLPs for H_2 activation because it possesses a higher HIA than $\text{B}(\text{C}_6\text{F}_5)_3$ but has a diminished Lewis acidity towards LBs more sterically demanding than H^- (e.g., Cl^-). The relatively low CIA allows facile access to $[\mathbf{4}]^+$ by abstraction of halide from (lutidine) BCl_2 by AlCl_3 or $\text{Na}[\text{BAR}^{\text{Cl}}]$.^[47] FLPs were not accessible on addition of PtBu_3 , PCy_3 or PPh_3 to $[\mathbf{4}]^+$. Instead, $[\text{Cl}_2\text{B}(2,6\text{-lutidine})(\text{PR}_3)]^+$ cations, which did not activate H_2 even on heating to 100 °C under H_2 at 4 atm, were formed. A FLP is formed on addition of extremely bulky PMes_3 to $[\mathbf{4}]^+$, but this FLP did not activate H_2 (4 atm in $o\text{-C}_6\text{H}_4\text{Cl}_2$) at 20 °C. At this temperature, equimolar mixtures of $[\mathbf{4}]^+/\text{PMes}_3$ displayed a slow decrease in the ^{11}B NMR resonance associated with $[\mathbf{4}]^+$ and a concomitant increase in a sharp ^{11}B NMR resonance at $\delta = 6.4$ ppm consistent with a four-coordinate boron environment. Full conversion to this new boron species can be achieved by heating equimolar $[\mathbf{4}]^+/\text{PMes}_3$ to 60 °C for 1 h [Eq. (8)]. The phosphonium cation $[\text{Mes}_3\text{PH}]^+$ was the only new phosphorus-containing species observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, indicating deprotonation of lutidine. The carbanion produced by deprotonation is stabilized by coordination to boron forming the four-membered boracycle $[(\text{CH}_2\text{-}\{\text{NC}_5\text{H}_3\text{Me}\})\text{BCl}_2]$ ($\mathbf{5}$). Coordination of 2,6-lutidine to the highly Lewis acidic $\{\text{BCl}_2\}^+$ fragment significantly reduced the pK_a of the *ortho*-methyl protons enabling deprotonation by the bulky, but only moderately basic phosphine. Compound $\mathbf{5}$ can be independently synthesised, but requires the strong base $n\text{BuLi}$ to deprotonate 2,6-lutidine; subsequent transmetalation with BCl_3 provides $\mathbf{5}$, analogous to the formation of $[(\text{CH}_2\{\text{NC}_5\text{H}_4\})\text{BCy}_2]$.^[49]



Because the formation of $\mathbf{5}$ is slow at 20 °C, the ability of $[\mathbf{4}]^+/\text{PMes}_3$ to activate H_2 at elevated temperatures was investigated. Heating $[\mathbf{4}]^+/\text{PMes}_3$ to 100 °C under 4 atm of H_2 (in $o\text{-C}_6\text{H}_4\text{Cl}_2$) resulted in the formation of the boracycle $\mathbf{5}$

as the major product. However, resonances consistent with H_2 activation (specifically $\text{BHCl}_2(\text{lutidine})$) as a minor product were also observed by multinuclear NMR spectroscopy. Confirmation of dihydrogen activation was forthcoming from the reaction of D_2 with $[\mathbf{4}]^+/\text{PMes}_3$, which produced $[\text{Mes}_3\text{PD}]^+$ (a 1:1:1 triplet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum). The ^{11}B NMR spectrum now showed the resonance for $\mathbf{5}$ and a broad signal centred at $\delta = 1$ ppm attributable to (lutidine) BDCl_2 . Importantly, $\mathbf{5}$ did not react with H_2 at 100 °C (4 atm, 18 h),^[39] confirming that H_2 activation is by the FLP formed from the borenium cation $[\mathbf{4}]^+$ and PMes_3 .

FLPs containing phenyl-ligated borenium cations: Mechanistically, extensive computational work indicated that the activation of H_2 by $\text{B}(\text{C}_6\text{F}_5)_3/\text{LBs}$ proceeds through a concerted process involving “encounter complexes”.^[50] However, an alternative mechanism involving intramolecular heterolytic cleavage of H_2 across a B–C bond followed by subsequent intermolecular deprotonation cannot currently be precluded.^[51] Furthermore, Piers et al. have recently demonstrated that the highly electrophilic perfluoropenta phenylborole activates H_2 without an additional equivalent of LB, with H_2 heterolytically cleaved across the B–C bond.^[52] To probe if H_2 cleavage would occur with a borenium cation containing a B–C_{aryl} moiety, $\text{PhBCl}_2(\text{lutidine})$ was synthesized, and halide abstraction effected with AlCl_3 or $\text{Na}[\text{BAR}^{\text{Cl}}]$. Whilst pure $[\text{PhBCl}(\text{lutidine})]^+$ ($[\mathbf{6}]^+$) was not isolable despite numerous efforts, $[\mathbf{6}]^+$ can be produced in situ as the major species (>90 % by multinuclear NMR spectroscopy). In the absence of a LB, $[\mathbf{6}]^+$ displayed no reaction towards H_2 at 20 °C or 100 °C (4 atm of H_2 , $o\text{-C}_6\text{H}_4\text{Cl}_2$). The addition of one equivalent of PMes_3 to $[\mathbf{6}]^+$ produced a FLP that also undergoes slow deprotonation of a methyl group of lutidine leading to boracycle $\mathbf{7}$ [Eq. (9)]. At high temperatures (100 °C), D_2 activation was observed with $[\mathbf{6}]^+/\text{PMes}_3$ to form (lutidine) $\text{BD}(\text{Ph})\text{Cl}$ and $[\text{DPMes}_3]^+$, but again the major product was the boracycle $\mathbf{7}$, formed by deprotonation of lutidine. With no observed difference in the propensity of $[\text{Cl}_2\text{B}(\text{lutidine})]^+$ and $[\text{PhBCl}(\text{lutidine})]^+$ to activate H_2 , this suggests that both FLPs activate H_2 through a similar mechanism, presumably involving an encounter complex.



Conclusion

Borenium cations that possess a wide range of HIAs are easily accessible, which makes them readily tuneable catalysts for hydrogenations. The calculated relative HIA is a useful tool for assessing hydride-transfer ability, a key step in ionic hydrogenation.^[53] The HIA of borenium cations is

highly dependent on both the degree of steric crowding in the four-coordinate neutral borane (HBX_2L) and the electrophilicity of the borenium cation. Borenium cations with high (relative to $\text{B}(\text{C}_6\text{F}_5)_3$) HIAs can be readily accessed by using the weak π -donor ligands Cl^- and/or Ph^- with lutidine as the LB. These borenium cations activate H_2 in FLPs with PMe_3 , but due to their fierce electrophilicity, H_2 cleavage occurs concomitantly with deprotonation of lutidine to form boracycles $[(\text{CH}_2\{\text{NC}_5\text{H}_3\text{Me}\})\text{BCl}(\text{Y})]$. FLPs containing high-HIA borenium cations that are stable to deactivation reactions, such as ligand deprotonation, are currently under investigation.

Acknowledgements

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