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The Hydride-Ion Affinity of Borenium Cations and Their Propensity to Activate H_2 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 $[CatB(PtBu_3)]^+$ has a lower hydride-ion affinity (HIA) than $B(C_6F_5)_3$. This resulted in H_2 activation being energetically unfavourable in a FLP with the strong base $PtBu_3$. However, ligand disproportionation of $CatBH(PtBu_3)$ at 100 °C enabled trapping of H_2 activation products. DFT calculations at the M06-2X/6-311G(d,p)/PCM (CH_2Cl_2) level revealed that replacing catechol with chlorides significantly increases the chloride-ion affinity (CIA) and HIA. Dichloro–borenium cations, $[Cl_2B(amine)]^+$, were calculated to have considerably greater HIA than $B(C_6F_5)_3$. 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 $[Y(Cl)B(2,6\text{-lutidine})]^+$ (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 $[(CH_2\{NC_5H_3Me\})B(Cl)Y]$ and $[HPMes_3]^+$. When equimolar $[Y(Cl)B(2,6\text{-lutidine})]^+/P(mesityl)_3$ was heated under H_2 (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 H_2 and the catalytic reduction of unsaturated and aromatic moieties.[4–16] A plethora of Lewis bases, ranging from moderately basic $(2,4,6\text{-trimethylphenyl})_3P$ ($PMes_3$) to strongly basic N-heterocyclic carbenes (NHCs), have been successfully employed in FLP H_2 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 $B(C_6F_5)_3$. This is due to a minimum cumulative Lewis acid (LA)/base (LB) strength being a prerequisite for H_2 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 $B(C_6F_5)_3$, can shift the H_2 activation equilibrium [Eq. (1)] drastically towards the neutral starting materials, even when using a strong LB.[23–25]

$$\mathrm{LA} + \mathrm{LB} \rightleftharpoons \mathrm{LA{-}{-}{-}LB} \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} [\mathrm{LA\text{-}H}]^- [\mathrm{LB\text{-}H}]^+ \qquad (1)$$

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-$C_6H_4S_2$) ligated borenium cations,[30] and are interested in using these and other borenium cations in FLPs for H_2 activation. Borenium cations can be more electrophilic than $B(C_6F_5)_3$, and high Lewis acidity towards hydride ions should enable the extension of FLP activation of H_2 towards weaker LBs. Recognizing the potential of highly electrophilic cationic LAs in FLPs, Müller et al. have recently reported that a silicenium cation $[(Me_5C_6)_3Si]^+$ formed an FLP with $PMes_3$ that rapidly cleaved H_2. However, this FLP did not activate H_2 with weakly basic $P(C_6F_5)_3$.[17] Borenium cations are valence isoelectronic to silicenium cations, and a first indication that they could activate H_2 came from the work of Vedejs et al., who observed deuterium incorporation on heating **1** under a D_2 atmosphere (Figure 1, top).[31] Although the heterogeneous nature of this system precluded mechanistic elucidation, H_2 activation by a FLP was one possibility. Insight into the hydride-ion affinity (HIA) of borenium cations, particularly relative to $B(C_6F_5)_3$, is limited. One exception comes from the work of Stephan et al., which synthesized [CatB-

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[a] Dr. E. R. Clark, A. Del Grosso, Dr. M. J. Ingleson
Department of Chemistry, University of Manchester
Manchester, M13 9PL (U.K.)
E-mail: Michael.ingleson@manchester.ac.uk

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.

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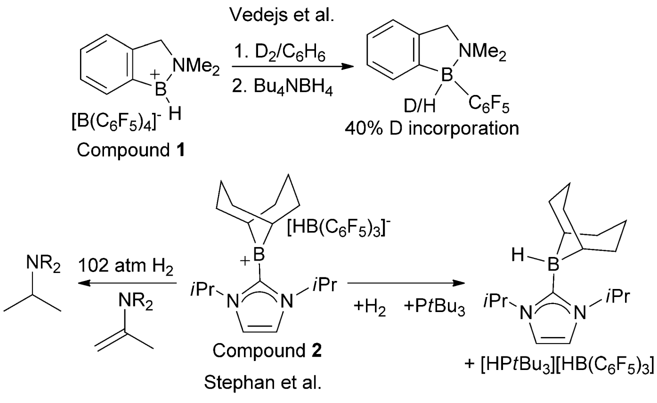


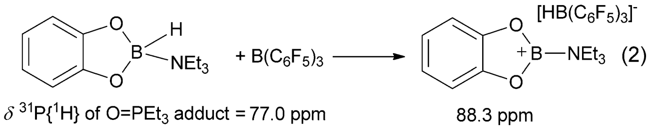
Figure 1. Recent examples of H$_2$ activation by borocations and the application of **2** as a catalyst for the hydrogenation of enamines.

(P*t*Bu$_3$)][HB(C$_6$F$_5$)$_3$] by hydride-ion transfer from CatBH(P*t*Bu$_3$) to B(C$_6$F$_5$)$_3$.[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$_6$F$_5$)$_3$ 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$_6$F$_5$)$_3$ 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$_6$F$_5$)$_3$. 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$_6$F$_5$)$_3$ with hydride transfer observed upon addition of B(C$_6$F$_5$)$_3$ to CatBH(amine) to form [CatB(amine)][HB(C$_6$F$_5$)$_3$] (amine = Et$_3$N 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$_3$PO upon coordination to [CatB(NEt$_3$)]$^+$ indicates that this borenium cation is more Lewis acidic towards Et$_3$PO than B(C$_6$F$_5$)$_3$ [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$_6$F$_5$)$_3$ (FIA of SbF$_5$ = 489 compared to a FIA of 444 kJ mol^{-1} for B(C$_6$F$_5$)$_3$).[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$_3$PO$^-$, 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$_6$F$_5$)$_{3-x}$(OC$_6$F$_5$)$_x$ (x = 0–3) series with respect to Et$_3$PO and Et$_3$PS LBs.[38]



(2)

Although catechol–borenium cations are less Lewis acidic towards hydride than B(C$_6$F$_5$)$_3$, 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 P*t*Bu$_3$/[CatB(P*t*Bu$_3$)][AlCl$_4$] (**3**) was investigated. It displayed broad ^{31}P{^{1}H} and ^{11}B NMR resonances (δ = 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 °C revealed the presence of two major species, the borenium cation **3** and free P*t*Bu$_3$.[39] Thus, compound **3** and P*t*Bu$_3$ exist as a FLP in equilibrium with its Lewis adduct [CatB(P*t*Bu$_3$)$_2$]$^+$. The addition of H$_2$ (ca. 4 atm) to equimolar **3**/P*t*Bu$_3$ in C$_6$H$_4$Cl$_2$ (+10% C$_6$D$_6$) led to no reaction at 25 °C (18 h). However, heating this solution to 100 °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**/P*t*Bu$_3$ are [HP*t*Bu$_3$]$^+$ and CatBH(P*t*Bu$_3$), but the latter is in equilibrium with CatBH and P*t*Bu$_3$. This system is further complicated by CatBH/P*t*Bu$_3$ disproportionating rapidly

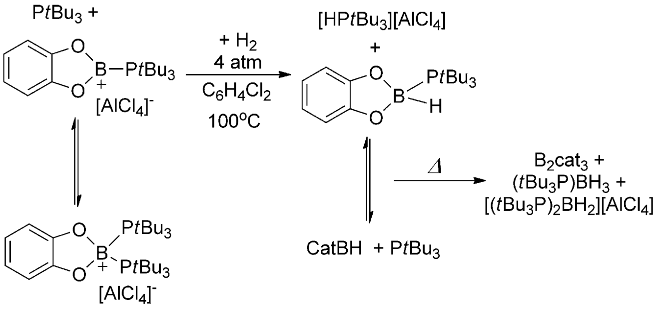
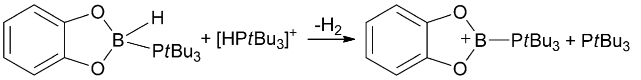


Figure 2. Schematic representation of the equilibrium with **3**/P*t*Bu$_3$ and activation of H$_2$ with subsequent ligand disproportionation.

at 100 °C[40] to form products including B_2cat_3 and $(tBu_3P)BH_3$ (determined by ^{11}B NMR spectroscopy).[41,42] Unambiguous confirmation of dihydrogen activation was provided by the exposure of equimolar **3**/P*t*Bu$_3$ to D_2. This led to the formation of $[DPtBu_3]^+$ (a 1:1:1 triplet in the $^{31}P\{^1H\}$ NMR spectrum with P–D coupling of 66 Hz) and broad ^{11}B NMR resonances devoid of B–H coupling.

The requirement for high temperatures before H_2 activation observed with **3**/P*t*Bu$_3$ is attributed to the activation of H_2 being energetically unfavourable due to the lower HIA of $[CatB(PtBu_3)]^+$ (relative to $B(C_6F_5)_3$). A low equilibrium concentration of H_2 activation products is presumably present and the rapid ligand disproportionation of CatBH/P*t*Bu$_3$ that takes place at 100 °C and drives H_2 activation to completion. This hypothesis is supported by the reverse reaction, that is, the addition of $[HPtBu_3][B(C_6H_3Cl_2)_4]$ to CatBH-(P*t*Bu$_3$), evolving H_2 at 20 °C [Eq. (3)] ($[B(C_6H_3Cl_2)_4]^-$ is termed $[BAr^{Cl}]^-$ from here on).



(3)

Assessment of relative HIAs and chloride-ion affinities (CIAs): Seeking a borenium cation that possesses a greater HIA than $B(C_6F_5)_3$, 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 $[HBEt_3]^-$, 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 phosphenium cations, which led to >100 kcal mol^{-1} overestimation of FIA.[45] CIAs relative to $AlCl_3$ were also estimated by using an approach based on the transfer of chloride from $[AlCl_4]^-$ to the borenium cation [Eq. (6)].[46] This value is important for determining accessibility of the borenium cation by halide abstraction.

$$[X_2BL]^+ + [HBEt_3]^- \xrightarrow{\Delta H_{HIA}} X_2HBL + BEt_3 \qquad (4)$$

$$X_3B + [HBEt_3]^- \xrightarrow{\Delta H_{HIA}} X_3BH + BEt_3 \qquad (5)$$

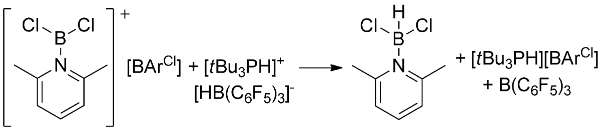
$$[X_2BL]^+ + [AlCl_4]^- \xrightarrow{\Delta H_{CIA}} X_2ClBL + AlCl_3 \qquad (6)$$

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, $[CatBNEt_3]^+$ has an enhanced CIA versus the thiocatechol analogue $[(o\text{-}C_6H_4S_2)BNEt_3]^+$ 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 $[Cl_2B(2,6\text{-lutidine})]^+$, (**[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)BCl_3. Steric crowding in four coordinate (at boron) (*i*Pr–NHC)BH(C_8H_{14}) presumeably 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.

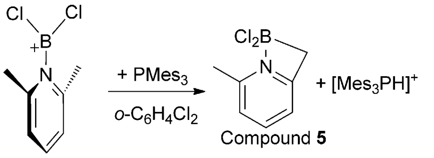
	HIA [kcal mol^{-1}]	CIA [kcal mol^{-1}]
	M06-2X/6-311G(d,p) /PCM$_{(CH_2Cl_2)}$ ΔH	M06-2X/6-311G(d,p) /PCM$_{(CH_2Cl_2)}$ ΔH
neutral boranes		
BEt_3	0.0	–
$B(C_6F_5)_3$	−41.0	–
borenium cations		
$[CatB{-}PtBu_3]^+$, **[3]**$^+$	−33.0	27.1
$[CatB{-}NEtiPr_2]^+$	−37.9	30.2
[2]$^+$	−41.6	–
$[CatB{-}NEt_3]^+$	−43.6	21.8
$[(o\text{-}C_6H_4S_2)B{-}NEt_3]^+$	−45.8	27.7
$[PhBCl(2,6\text{-lut})]^+$, **[6]**$^+$	−47.8	26.8
$[Cl_2B{-}NEtiPr_2]^+$	−61.0	17.3
$[Cl_2B(2,6\text{-lut})]^+$, **[4]**$^+$	−61.7	20.7
$[Cl_2B{-}NEt_3]^+$	−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 $AlCl_3$ consistent with the chloride abstraction experimentally observed on combination of $X_2BCl(L)$ and $AlCl_3$, forming $[X_2BL][AlCl_4]$.[47,48] The calculated CIAs between borenium cations were also internally consistent, with chloride transfer observed from $CatB(NEt_3)Cl$ to $[Cl_2B(2,6\text{-lut})]^+$. Of more importance to this work is the accuracy of the relative HIA of $B(C_6F_5)_3$ and borenium cations. Cation **[4]**$^+$ has a HIA 20.7 kcal mol^{-1} greater than that of $B(C_6F_5)_3$; thus **[4]**$^+$ should abstract hydride from $[HB(C_6F_5)_3]^-$. Pleasingly, mixing $[HPtBu_3][HB(C_6F_5)_3]$ and **[4][BAr^{Cl}]** resulted in rapid formation of $BCl_2H(2,6\text{-lut})$, $[tBu_3PH][BAr^{Cl}]$ and $B(C_6F_5)_3$ [Eq. (7)]. This confirms that borenium cations can have higher HIAs than $B(C_6F_5)_3$. These calculations also correctly predicted the observed abstraction of hydride from $CatB(PtBu_3)H$ by $B(C_6F_5)_3$. However, $[CatB(NEt_3)]^+$ and **[2]**$^+$ were both calculated to have HIAs greater than $B(C_6F_5)_3$ (by 2.6 and 0.6 kcal mol^{-1}, respectively). Repeating the HIA calculations for BEt_3, $B(C_6F_5)_3$ and $[CatB(NEt_3)]^+$ using a basis set including a diffuse function (M06-2X/6-311G+(d,p)/PCM(CH_2Cl_2)) to more accurately model the anionic component resulted in only minor differences. At this level of theory, the HIA of $B(C_6F_5)_3$ was effectively identical to $[CatB(NEt_3)]^+$ (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 **[4]**$^+$ and $B(C_6F_5)_3$.



[4][BAr^{Cl}] (7)

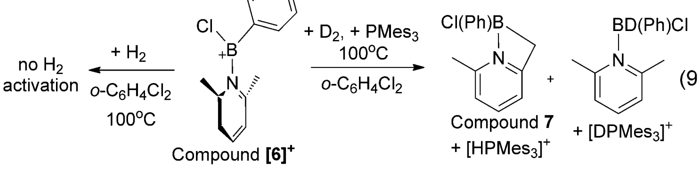
FLPs containing di-chloride-ligated borenium cations: Cation **[4]**$^+$ was selected to incorporate into FLPs for H_2 activation because it possesses a higher HIA than $B(C_6F_5)_3$ but has a diminished Lewis acidity towards LBs more sterically demanding than H^- (e.g., Cl^-). The relatively low CIA allows facile access to **[4]**$^+$ by abstraction of halide from (lutidine)BCl_3 by $AlCl_3$ or $Na[BAr^{Cl}]$.[47] FLPs were not accessible on addition of $PtBu_3$, PCy_3 or PPh_3 to **[4]**$^+$. Instead, $[Cl_2B(2,6\text{-lutidine})(PR_3)]^+$ 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 **[4]**$^+$, but this FLP did not activate H_2 (4 atm in o-$C_6H_4Cl_2$) at 20 °C. At this temperature, equimolar mixtures of **[4]**$^+$/$PMes_3$ displayed a slow decrease in the ^{11}B NMR resonance associated with **[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 **[4]**$^+$/$PMes_3$ to 60 °C for 1 h [Eq. (8)]. The phosphonium cation $[Mes_3PH]^+$ was the only new phosphorus-containing species observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating deprotonation of lutidine. The carbanion produced by deprotonation is stabilized by coordination to boron forming the four-membered boracycle $[(CH_2\text{-}\{NC_5H_3Me\})BCl_2]$ (**5**). Coordination of 2,6-lutidine to the highly Lewis acidic $\{BCl_2\}^+$ fragment significantly reduced the pK_a of the *ortho*-methyl protons enabling deprotonation by the bulky, but only moderately basic phosphine. Compound **5** can be independently synthesised, but requires the strong base nBuLi to deprotonate 2,6-lutidine; subsequent transmetalation with BCl_3 provides **5**, analogous to the formation of $[(CH_2\{NC_5H_4\})BCy_2]$.[49]



Compound **5** (8)

Because the formation of **5** is slow at 20 °C, the ability of **[4]**$^+$/$PMes_3$ to activate H_2 at elevated temperatures was investigated. Heating **[4]**$^+$/$PMes_3$ to 100 °C under 4 atm of H_2 (in o-$C_6H_4Cl_2$) resulted in the formation of the boracycle **5** as the major product. However, resonances consistent with H_2 activation (specifically $BHCl_2$(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 **[4]**$^+$/$PMes_3$, which produced $[Mes_3PD]^+$ (a 1:1:1 triplet in the $^{31}P\{^1H\}$ NMR spectrum). The ^{11}B NMR spectrum now showed the resonance for **5** and a broad signal centred at $\delta = 1$ ppm attributable to (lutidine)$BDCl_2$. Importantly, **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 **[4]**$^+$ and $PMes_3$.

FLPs containing phenyl-ligated borenium cations: Mechanistically, extensive computational work indicated that the activation of H_2 by $B(C_6F_5)_3$/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, $PhBCl_2$(lutidine) was synthesized, and halide abstraction effected with $AlCl_3$ or $Na[BAr^{Cl}]$. Whilst pure [PhBCl(lutidine)]$^+$ (**[6]**$^+$) was not isolable despite numerous efforts, **[6]**$^+$ can be produced in situ as the major species (>90% by multinuclear NMR spectroscopy). In the absence of a LB, **[6]**$^+$ displayed no reaction towards H_2 at 20 °C or 100 °C (4 atm of H_2, o-$C_6H_4Cl_2$). The addition of one equivalent of $PMes_3$ to **[6]**$^+$ produced a FLP that also undergoes slow deprotonation of a methyl group of lutidine leading to boracycle **7** [Eq. (9)]. At high temperatures (100 °C), D_2 activation was observed with **[6]**$^+$/$PMes_3$ to form (lutidine)BD(Ph)Cl and $[DPMes_3]^+$, but again the major product was the boracycle **7**, formed by deprotonation of lutidine. With no observed difference in the propensity of $[Cl_2B(\text{lutidine})]^+$ and $[PhBCl(\text{lutidine})]^+$ to activate H_2, this suggests that both FLPs activate H_2 through a similar mechanism, presumably involving an encounter complex.



Compound **[6]**$^+$ Compound **7** + $[HPMes_3]^+$ + $[DPMes_3]^+$ (9)

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 $B(C_6F_5)_3$) 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 $PMes_3$, but due to their fierce electrophilicity, H_2 cleavage occurs concomitantly with deprotonation of lutidine to form boracycles $[(CH_2\{NC_5H_3Me\})BCl(Y)]$. 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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[1] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50; *Angew. Chem. Int. Ed.* **2010**, *49*, 46.
[2] D. W. Stephan, *Chem. Commun.* **2010**, *46*, 8526.
[3] G. C. Welch, R. R. San-Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124.
[4] D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740.
[5] P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050.
[6] P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701.
[7] P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem.* **2008**, *120*, 7654; *Angew. Chem. Int. Ed.* **2008**, *47*, 7543.
[8] K. V. Axenov, G. Kehr, R. Fröhlich, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 3454.
[9] V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117.
[10] H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966.
[11] C. F. Jiang, O. Blacque, H. Berke, *Chem. Commun.* **2009**, 5518.
[12] G. Eros, H. Mehdi, I. Papai, T. A. Rokob, P. Kiraly, G. Tarkanyi, T. Soos, *Angew. Chem.* **2010**, *122*, 6709; *Angew. Chem. Int. Ed.* **2010**, *49*, 6559.
[13] D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, M. Ullrich, *Inorg. Chem.* **2011**, *50*, 12338.
[14] D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130.
[15] Z. M. Heiden, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 5729.
[16] T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 4088.
[17] A. Schäfer, M. Reissmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem.* **2011**, *123*, 12845; *Angew. Chem. Int. Ed.* **2011**, *50*, 12636.
[18] A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 8826.
[19] G. Ménard, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 8272.
[20] F. Bertini, V. Lyaskovskyy, B. J. J. Timmer, F. J. J. d. Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2012**, *134*, 201.
[21] T. A. Rokob, A. Hamza, I. Papai, *J. Am. Chem. Soc.* **2009**, *131*, 10701.
[22] S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem.* **2010**, *122*, 1444; *Angew. Chem. Int. Ed.* **2010**, *49*, 1402.
[23] G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, 3407.
[24] A. M. Chapman, M. F. Haddow, J. P. H. Orton, D. F. Wass, *Dalton Trans.* **2010**, *39*, 6184.
[25] A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2010**, *132*, 3301.
[26] P. Koelle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399.
[27] W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem.* **2005**, *117*, 5142; *Angew. Chem. Int. Ed.* **2005**, *44*, 5016.
[28] T. S. De Vries, A. Prokofjevs, E. Vedejs, *Chem. Rev.* **2012**, *112*, 4246.
[29] A. Prokofjevs, A. Boussonniere, L. Li, H. Bonin, E. Lacote, D. P. Curran, E. Vedejs, *J. Am. Chem. Soc.* **2012**, *134*, 12281.
[30] S. A. Solomon, A. Del Grosso, E. R. Clark, V. Bagutski, J. J. W. McDouall, M. J. Ingleson, *Organometallics* **2012**, *31*, 1908.
[31] T. S. De Vries, A. Prokofjevs, J. N. Harvey, E. Vedejs, *J. Am. Chem. Soc.* **2009**, *131*, 14679.
[32] M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303.
[33] J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728.
[34] M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530.
[35] V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225.
[36] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.
[37] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533.
[38] G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685.
[39] See Supporting Information.
[40] S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, J. C. Calabrese, *Inorg. Chem.* **1993**, *32*, 2175.
[41] K. Burgess, W. A. v. d. Donk, S. A. Westcott, T. B. Marder, R. T. Naker, J. C. Calabrese, *J. Am. Chem. Soc.* **1992**, *114*, 9350.
[42] R. B. Coapes, F. E. S. Souza, M. A. Fox, A. S. Batsanov, A. E. Goeta, D. S. Yufit, M. A. Leech, J. A. K. Howard, A. J. Scott, W. Clegg, T. B. Marder, *Dalton Trans.* **2001**, 1201.
[43] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
[44] M. T. Mock, R. G. Potter, D. M. Camaioni, J. Li, W. G. Dougherty, W. S. Kassel, B. Twamley, D. L. DuBois, *J. Am. Chem. Soc.* **2009**, *131*, 14454.
[45] J. M. Slattery, S. Hussein, *Dalton Trans.* **2012**, *41*, 1808.
[46] A. Kraft, J. Beck, I. Krossing, *Chem. Eur. J.* **2011**, *17*, 12975.
[47] A. Del Grosso, M. D. Helm, S. A. Solomon, D. Caras-Quintero, M. J. Ingleson, *Chem. Commun.* **2011**, *47*, 12459.
[48] A. Del Grosso, P. J. Singleton, C. A. Muryn, M. J. Ingleson, *Angew. Chem.* **2011**, *123*, 2150; *Angew. Chem. Int. Ed.* **2011**, *50*, 2102.
[49] J. Vergnaud, T. Ayed, K. Hussein, L. Vendier, M. Grellier, G. Bouhadir, J.-C. Barthelat, S. Sabo-Etienne, D. Bourissou, *Dalton Trans.* **2007**, 2370.
[50] I. Bakó, A. Stirling, S. Balint, I. Papai, *Dalton Trans.* **2012**, *41*, 9023, and references therein.
[51] R. Rajeev, R. B. Sunoj, *Chem. Eur. J.* **2009**, *15*, 12846.
[52] C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 9604.
[53] After submission of this article, Crudden et al. reported the superior reducing ability of PinB(amine)H relative to $[HB(C_6F_5)_3]^-$ (pin = pinacolato) indicating that $[PinB(amine)]^+$ borenium cations have a lower HIA than $B(C_6F_5)_3$, see: P. Eisenberger, A. M. Bailey, C. M. Crudden, *J. Am. Chem. Soc.* **2012**, *134*, 17384.

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