A family of N-heterocyclic carbone-stabilized borenium ions for metal-free imine hydrogenation catalysis†

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This manuscript probes the steric and electronic attributes that lead to “frustrated Lewis pair” (FLP)-type catalysis of imine hydrogenation by borenium ions. Hydride abstraction from (IiPr)BC8H14 [B(C6F5)4] 2 prompts intramolecular C–H bond activation to give (CHN)2(IiPr) (CMe2CH2)CB(C6F5)2 3, defining an upper limit of Lewis acidity for FLP hydrogenation catalysis. A series of seven N-heterocyclic carbene–borane (NHC–borane) adducts ([R’CNR2]Cl(BC6H5)2) ([R’ = H, R = Me; R’ = Me 9a, Cl, 10a] and ([H(C)2NMe1NR(3)]Cl)(BC6H5)2) ([R’ = tBu, 6a, Ph 7a]) are prepared and converted to corresponding borenium salts. These species are evaluated as catalysts for metal-free imine hydrogenation at room temperature. Systematic tuning of the carbene donor for the hydrogenation of archetypal substrate N-benzylidene-tert-butylamine achieves the highest reported turn-over frequencies for FLP-catalyzed hydrogenation at amongst the lowest reported catalyst loadings. The most active NHC–borenium catalyst of this series, derived from 10a, is readily isolable, crystallographically characterized and shown to be effective in the hydrogenation catalysis of functional group-containing imines and N-heterocycles.

Introduction

As the global consciousness awakens to the environmental and fiscal costs associated with energy and material-intensive chemical processes, the development of new and effective catalytic strategies grows ever more significant. The hydrogenation of unsaturated bonds is one such chemical transformation that is employed on a terrific industrial scale.1–4 Currently these processes employ highly effective transition metal catalysts despite oft associated high cost, toxicity and significant carbon footprint. These drawbacks have led to the intense pursuit of alternative or complimentary technologies. For example, hydrogenation catalysis by cheap and non-toxic transition metals such as iron3–5 and cobalt6,7 as well as early metals such as titanium8,9 and calcium10 has drawn considerable attention. Our group14–23 and others24–49 have focused on main-group alternatives motivated by our report of metal-free hydrogen activation by a linked phosphino-borane.44 Indeed, soon after this initial report, we described the use of “frustrated Lewis pairs” (FLPs) in the catalytic hydrogenation of imines and protected nitriles.23 This prompted a flurry of developments in FLP hydrogenation catalysis. While substrate scope has since been dramatically broadened, the catalytic activities of FLP systems and the catalyst loadings required are not yet competitive with transition metal catalysts. Perhaps more importantly, the synthetic challenge of preparing electrophilic boranes limits the range of potential catalysts that are readily accessible for a systematic evaluation of structure–activity relationships. Indeed, although studies involving families of closely related FLP hydrogenation catalysts are rare,29,38,39,42 some examples in the literature suggests that subtle changes to FLP catalysts can have a dramatic impact on activity and selectivity. For example, the group of Soós and co-workers has shown that substitution of one C6F5 in B(C6F5)3 with the bulkier mesityl group effects selectivity control through size exclusion.34,35 Moreover, careful choice of Lewis base in FLP hydrogenation catalysis has extended the substrate scope to include silyl enol ethers,77 olefins18,33 and most recently ketones and aldehydes.41,44

Borenium ions are three-coordinate boron cations.45–47 These relatively underexplored Lewis acids have attracted recent attention for use in catalysis48–55 and selective carboborations and haloborations.56–58 In an earlier communication, our group showed that an N-heterocyclic carbene-stabilized borenium salt [(IiPr)BC6H5] [B(C6F5)3] [(IiPr = 1,3-di-isopropylimidazol-2-ylidene) can be used as a catalyst for the metal-free hydrogenation of imines and enamines.55 In this case, the borenium cation and the imine act as an FLP to cleave H2. This affords an NHC–borane that delivers hydride to a transient iminium ion.
Borenium-based catalyst 1b derives its Lewis acidity from a cationic charge rather than electron-withdrawing fluororayl groups on boron. Moreover, the precursor NHC–borane adduct is robust and easily accessible. During the review process of this paper Crudden and co-workers described triazolium derived borenium cations as catalysts.89

Herein, we exploit our previous findings to access a family of FLP catalysts. The reactivity of these borenium cations is evaluated in the metal-free hydrogenation catalysis of imines and N-heterocycles. This systematic study of the steric and electronic attributes of NHC–borenium catalysts provides insight into the structure–activity relationship of this new class of FLP hydrogenation catalyst.

Results and discussion

Our initial efforts to enhance reactivity with respect to previously reported catalyst 1b focused on the incorporation of electron withdrawing CsF2 substituents in NHC–boronions. To this end, the reaction of 1,3-di-tert-butylimidazol-2-ylidene (tBu) with HB(C6F5)2 led to the formation of NHC–borane adduct (tBuHB(C6F5)2 2 (Scheme 2), which was isolated in 76% yield. Crystallographic characterization revealed the anticipated pseudo-tetrahedral geometry about boron, an average C_NHC–B bond length of 1.645(4) Å and an average B–C_{CsF2} bond length of 1.639(4) Å (Fig. 1(a)). The expected upfield doublet for 2 is observed by 11B NMR spectroscopy at −22.9 ppm with a $J_{B-H}$ coupling of 88 Hz. The $^1$H NMR and $^{19}$F NMR spectra indicate hindered rotation about the C_NHC–B bond in 2 on the NMR time scale. Broad and inequivalent resonances were observed for the tert-butyl protons and fluorine atoms at room temperature; however, these were resolved upon cooling to $-40 °C$.

Attempts to generate an NHC–borenium ion derived from 2 via treatment with the hydride abstraction reagents [Ph3C][B(C6F5)4], Me3SiOTf or HOTf showed no reaction. This stands in contrast to the facile hydride donation typically demonstrated by NHC–boranes.86,89 However, upon heating 2 with HNTf2 in toluene to >100 °C for four days the clean conversion to a new product was evident from the appearance of the $^1$B resonance at −14.8 ppm. $^1$H NMR spectroscopy showed sharp singlet resonances at 0.86 ppm and 1.04 ppm and a broad singlet resonance at 1.80 ppm integrating in a 9 : 6 : 2 ratio.

These combined NMR data suggest the new species (CHN)2(tBu)(CMe2CH2)CBBr2 is derived from (1BuHB(C6F5)2 via transient generation of a cation and subsequent C–H activation (Scheme 2). A crystallographic study of 3 confirmed its bicyclic nature (Fig. 1(b)). This species is similar to compounds (CHN)2(tBu)(CMe2CH2)CBBr2 and (CHN)2(tBu)(CMe2CH2)CBBr2 recently reported by Braunschweig and co-workers. The formation of 3 is thought to proceed via transient generation of a cation and subsequent C–H activation (Scheme 2). Similar borylations of aliphatic groups by donor stabilized borenium ions have been reported by Prokofjevs and Vedejs.72

The C–H activation that yields 3 suggests that the proposed CsF2-substituted borenium ion derived from 2 is too Lewis acidic for application in catalysis. This prompted us to further examine 9-BBN based borenium cations. To this end 9-BBN was reacted with 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene (Idipp) at 60 °C for one hour to afford Idipp–borane adduct 4a in 79% yield (Scheme 3). Compound 4a exhibits a broad $^1$B NMR signal at −15.3 ppm. Reaction of 4a with [Ph3C][B(C6F5)4] at 45 °C overnight results in the generation of Ph3CH and the quantitative conversion of the NHC–borane to a new species as evidenced by $^1$B NMR signals at 82.6 ppm and −16.6 ppm. These are consistent with the formation the borenium–borate salt $[\text{Idipp}][\text{B(C6F5)4}]$ 4b. Alternatively, treatment of 4a with tBuN=CHPh and the addition of a stoichiometric equivalent of [tBu3P][B(C6F5)4] results in generation of 4b with...
To further probe the steric and electronic factors impacting on the reactivity of NHC–borenium cations, a series of NHC-9-BBN adducts were prepared exercising judicious variation of the NHC. This was achieved by either directly reacting 9-BBN dimer with the isolated carbene or by reacting 9-BBN dimer with a carbene generated in situ through the combination of an imidazolidinum salt with K[N(SiMe3)2]. This latter one-pot approach is similar to that described by Brahmi et al. to prepare a series of NHC–BH3 compounds. A series of seven adducts including ((R′CNR)2C)BC8H14 (R′ = H, R = dipp 4a, Mes 5a, Me 8a; R = Me R′ = Me 9a, Cl, 10a) and ((HC)(NMMe)(NR)C)BC8H14 (R = tBu, 6a, Ph 7a) were prepared (Scheme 3). The NHC–borane adducts 4a–10a were isolated and purified via recrystallization from pentane or toluene in yields ranging from 72–95%. The spectral data reported for these compounds were as expected and crystallographic data for 5a, 7a, (see ESI†) and 8a–10a (Fig. 2) further corroborated these formulations.

Each of these adducts reacts with [Ph3C][B(C6F5)4] to give the corresponding borenium salt [((R′CNR)2C)BC8H14][B(C6F5)4] (R′ = H, R = dipp 4b, Mes 5b, 75–76 Me 8b; R = Me R′ = Me 9b, Cl, 10b) and [(HC)(NMMe)(NR)C]BC8H14[B(C6F5)4] (R = tBu, 6b, Ph 7b) concomitant with the generation of a stoichiometric amount of Ph3CH (Scheme 3). The most diagnostic spectroscopic change in each case is the appearance of a broad 11B resonance in the range of 81–88 ppm attributable to a three-coordinate B center. The expected resonances for the [B(C6F5)4]− anion were seen at −16.7 ppm. The species 10b was isolated as colorless crystals in 72% yield via recrystallization from CH2Cl2/pentane at −35 °C. Crystallographic data (Fig. 3) revealed trigonal planar geometry about the B center in the cation with a B–NHC bond length of 1.5768(3) Å similar to that observed for 1b (1.580(3) Å).67

For comparative purposes the phosphine–borane adduct (Me3P)(HBC8H14) (11) was also synthesized and isolated as colorless crystals in 82% yield. The 11B NMR signal was observed at −14.9 ppm and exhibited both B−H coupling of 88 Hz and B−P coupling of 48 Hz. The 31P{1H} resonance for 11 is at −13.0 ppm and possesses similar B−P coupling. Single crystal X-ray diffraction confirmed the formulation (see ESI†). In contrast to the carbene complexes described above, treatment of 11 with stoichiometric [Ph3C][B(C6F5)4] gave a complex mixture of products as evidenced by 31P{1H} and 11B NMR-spectroscopy.

**Table 1** Catalyst screening for the hydrogenation of N-benzylidene-tert-butylamine

| Entry | Cat. (mol%) | Yield (%) |
|-------|-------------|-----------|
| 1     | 1b (1)      | 35        |
| 2     | 4b (5)      | 0         |
| 3     | 5b (1)      | 0         |
| 4     | 6b (1)      | Trace     |
| 5     | 7b (1)      | 100       |
| 6     | 7b (0.5)    | 35        |
| 7     | 8b (1)      | 100       |
| 8     | 8b (0.5)    | 67        |
| 9     | 9b (0.5)    | 21        |
| 10    | 10b (0.5)   | 100       |
| 11    | 10b (0.25)  | 100       |
| 12    | 10b (0.1)   | 47        |
| 13    | 10b (0.15)  | 100 (83)  |

* Borenium salts were generated in situ by addition of [Ph3C][B(C6F5)4] to the corresponding borohydride precursor. Isolated 10b was used in entries 11–13. Determined by 1H NMR spectroscopy, isolated yields in parentheses. All reaction times were 30 min, except: 2 h reaction time.

**Scheme 3** General syntheses of NHC–boranes 4a–10a and generation of borenium salts 4b–10b.

![POV-ray depiction of (a) 8a (b) 9a (c) 10a](Image)

A: black, B: yellow-green, N: blue, H: grey, Cl: green. H-atoms except BH omitted for clarity.
Hydrogenation catalysis

Compounds 4b–10b were tested for catalytic activity using the hydrogenation of tBuN=CHPh as a comparative screen. A solution of each was generated in situ, added to the imine substrate and pressurized with 102 atm H₂ for 30 minutes. After the reaction, the extent of conversion to amine was assessed by ¹H NMR spectroscopy. These data reveal an inverse correlation between the steric demands of the NHC and the hydrogenation activity of the borenium catalyst (Table 1). The bulkiest catalyst 5b shows no catalytic activity, while the slightly less bulky catalyst 6b shows only trace conversion of imine to amine at 1 mol% catalyst loading after 30 minutes of reaction time. A sharp increase of catalytic activity is observed as the steric demands of the catalyst are further reduced. The previously reported catalyst 1b allows for 35% conversion to amine at 1 mol% catalyst loading after 30 minutes while catalysts 7b and 8b show quantitative conversion.

Reducing the loadings of these catalysts to 0.5 mol% under otherwise identical conditions reduced the conversions and demonstrated that the least bulky catalyst 8b effects 68% conversion while 7b and 9b reach only 35% and 21% conversion, respectively. In contrast, 10b gave complete conversion. Even when the loading was dropped to 0.25 mol% under otherwise identical conditions 10b gave complete conversion of imine to amine. Further reduction to 0.1 mol% gave 47% conversion representing a turn-over frequency (TOF) of 940 h⁻¹. A slight increase of catalyst loading to 0.15 mol% and an extension of the reaction time to 2 h at room temperature under 102 atm H₂ led to complete conversion to tBuNHCH₂Ph and the product could be isolated in 83% yield (Table 1, entry 13).

These observations reveal that the least sterically encumbered NHCs stabilize the most active borenium catalysts despite the fact that FLP reactivity hinges upon the steric protection of an acidic center. This suggests that the bulkier catalysts impede either H₂ activation or hydride delivery in the catalytic cycle. Since bulky NHC–borane 4a readily delivers hydride to an iminium ion it seems most likely that the bulkiest borenium ions are sterically prevented from generating the “encounter complex” with the imine that is required for H₂ activation. Similarly diminished reactivity has been observed for FLPs incorporating excessively bulky boranes. ²⁴ It is noteworthy that computations suggest that a donor–boron distance of 4.2 Å is necessary to effect heterolytic cleavage of H₂. ²⁵ Thus, it is reasonable to suggest that bulky peripheral substituents inhibit such a close approach.

Comparison of the isosteric catalysts 8b–10b reveals that reduced donation from the NHC to the B center has a positive impact on the catalytic activity. This is thought to result from an increase in the Lewis acidity at B. That being said, further reduction of the donor ability of the stabilizing ligand jeopardizes the stability of the borenium cation as evidenced by the efforts to abstract hydride from 11. Apparently the donor ability and steric demands of the NHC are suitably balanced in 10b as it provides, to our knowledge, the highest TOF reported to date.

| Entry | Substrate | Product | Yield |
|-------|-----------|---------|-------|
| 1     | ![Structure](image1.png) | ![Structure](image2.png) | 100⁶ (98) |
| 2     | ![Structure](image3.png) | ![Structure](image4.png) | 100 (82) |
| 3     | ![Structure](image5.png) | ![Structure](image6.png) | 39 |
| 4     | ![Structure](image7.png) | ![Structure](image8.png) | 100 (71) |
| 5     | ![Structure](image9.png) | ![Structure](image10.png) | 100 (95) |
| 6     | ![Structure](image11.png) | ![Structure](image12.png) | 0 |
| 7     | ![Structure](image13.png) | ![Structure](image14.png) | 100 (91) |
| 8     | ![Structure](image15.png) | ![Structure](image16.png) | 0 |
| 9     | ![Structure](image17.png) | ![Structure](image18.png) | 100 (87) |

a) Yields determined by ¹H NMR spectroscopy, isolated yields in parentheses. All reactions were carried out using 0.500 mmol substrate in CH₂Cl₂. Reaction times were 30 minutes. Catalyst loadings: 5 mol% except: ² 2.5 mol%.
for the metal-free hydrogenation of imines. With the optimized catalyst 10b in hand, a variety of N-containing unsaturated substrates were reduced affording products in high isolated yields (Table 2). In these cases a catalyst loading of 5 mol% was employed to ensure high conversions in 30 minutes and to overcome the impact of adventitious water. The imine o-C6H4-CH=NHPh2 is readily reduced (Table 2, entry 1) as is p-(MeO2C)C6H4-CH=NHPh2 (Table 2, entry 2). The latter stands in stark contrast to previous FLP hydrogenations where sterically unencumbered esters preclude or inhibit reductions using the borane B(C6F5)3.28 While the steric demands of C6H4-CH=NHCH3 slow imine reduction (Table 2, entry 3), the aniline-derived ketimines Ph(Me)C=CH=C=NH is readily hydrogenated to corresponding amines (Table 2, entries 4 and 5). In stark contrast, no hydrogenation of Ph(Me)C=CH=C=NPh and p-EtOCH2C6H4-CH=NH is observed (Table 2, entry 6). This was attributed to the greater basicity and lesser steric demands about the N-donor. 1,3,3-Trimethyl-2-methylideneindoline is hydrogenated to afford 1,2,3,3-tetramethylindoline (Table 2, entry 7), however 2,3,3-trimethylindololine is not reduced (Table 2, entry 8). Nonetheless, in contrast to previous FLP hydrogenations where sterically demanding substrates were reduced a

Conclusions

In this manuscript we have probed the electronic and steric parameters that impact on the ability of ligand stabilized borenium cations to act as metal-free hydrogenation catalysts. Although this catalysis proceeds via an FLP mechanism, perturbations that enhance the Lewis acidity at B or the steric demands of the NHC ligand can serve to deactivate the catalyst. At the same time, sterically unencumbered NHCs bearing electron withdrawing substituents enhance catalyst activity. Crudden and co-workers29 have very recently described related triazolium derived borenium cations and their use as catalysts for hydrogenation. Nonetheless, the present systematic examination of NHC stabilized borenium ion has led to catalysts that are highly efficient. Indeed the isolable catalyst 10b is an effective catalyst for imine and N-heterocycle reduction at low catalyst loadings and it affords the highest TOF yet reported for metal-free hydrogenation catalysis. Efforts are continuing to systematically develop borenium-based metal-free hydrogenation catalysts and to further broaden their applications.

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