The Synthesis of Unsymmetrical Diboron(5) Compounds and their Conversion to Diboron(5) Cations

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ABSTRACT: Reaction of bis-catecholatodiboron-NHC adducts, $B_2Cat_2(NHC)$, (NHC = IMe (tetramethylimidazol-2-ylidene), IMes (1,3-dimesitylimidazol-2-ylidene) or IDIPP (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)) with BCl_3 results in the replacement of the catecholato group bound to the four coordinate boron with two chlorides to yield diboron(5) Lewis acid-base adducts of formula $CatB$-$BCl_2(NHC)$. These compounds are precursors to diboron(5) monocations, accessed by adding $AlCl_3$ or $K[B(C_6F_5)_4]$ as halide abstraction agents in the presence of a Lewis base. The substitution of the chlorides of $CatB$-$BCl_2(NHC)$ for hydrides is achieved using Bu_3SnH and a halide abstracting agent to form 1,1-dihydrodiboron(5) compounds, $CatB$-$BH_2(NHC)$. Attempts to generate diboron(4) monocations of formula $[CatB$-$B(Y)(NHC)]^+$ (Y = Cl or H) led to the rapid formation of CatBY.

INTRODUCTION

Organoboron complexes are ubiquitous reagents in synthesis due to their utility in many functional group transformations. Many modern routes to organoboranes use diboron(4) compounds, e.g. bis-pinacolatodiboron B_2pin_2, thus these reagents have received considerable interest – as have diboron(5) derivatives that possess two distinct boron moieties with one being four coordinate.[1] These unsymmetrical diboron(5) species can be easily accessed by adding a neutral or anionic Lewis base to a $(RO)_2B$-$B(OR)_2$ precursor, quaternizing one boron center. Quaternization leads to polarization of the B-B σ bond and the resulting mixed sp^2/sp^3 diborons then react as sources of nucleophilic boron, reacting with an array of carbon electrophiles even in the absence of precious metal catalysts, thus providing a powerful route for forming C-B bonds.[2]

Until recently, the reactivity of diboron species as strong electrophiles had been mainly limited to highly reactive species such as B_2Cl_4. While B_2Cl_4 reacts with H_2, diborylates alkynes, alkenes and aromatics, it decomposes above 0 °C and its use historically had also been limited by a complex synthesis.[3] However, Braunschweig et al. has recently reported much simpler routes to B_2X_4 species.[4] Other symmetrical diboron(4) compounds that have appreciable electrophilicity have also been recently reported (e.g. $B_2(p\text{-tolyl})_4$) and shown to react with H_2.[5] In contrast, reports on the development of unsymmetrical diboron(4) and diboron(5) compounds that have significant electrophilicity are less common. Notable work in this area comes from Braunschweig et al., who during studies on the reactivity of Lewis bases with $R(X)B$-$B(X)R$ (X = halide, R = mesityl (Mes), tBu, NMe_2) synthesized an array of diboron(4)-based borenium cations (**A**, Figure 1).[6] More recently, Prokofjevs proposed the formation of a cationic sp^2-sp^3 diboron(5) cation formed from $[(L$-$BH_2)_2(\mu$-$H)]^+$ (L = $Me_3CCH_2NMe_2$), with calculations indicating that the diboron(5) cation $[L(H)_2B$-$BHL]^+$ is key in the intramolecular activation of aliphatic C-H bonds.[7] Other notable work in this area includes the formation an sp^2-sp^3 boryl-sub-

stituted boronium salt (**B**)[8] (Figure 1) and the unsymmetrical diboron(4) compound $pinBBMes_2$ (**C**), which reacts with CO, isocyanides and pyridine.[9] More recently, Wang and co-workers synthesized an N-heterocyclic carbene (NHC)-coordinated borylborenium cation (**D**), that when treated with H_2 resulted in addition of H_2 to the borenium center along with formation of Mes-BPin.[10] In addition to small-molecule activation, Himmel and co-workers reported that diboron(5) monocations can also dimerize to generate an unusual B_4 dication.[11]

These studies demonstrate that unsymmetrical diboron compounds are able to activate a range of small molecules in novel ways. However, the number of unsymmetrical and significantly electrophilic diboron compounds is still limited. Herein, we report the synthesis of readily available unsymmetrical diboron(5) compounds that can be converted to cationic diboron(5) species.
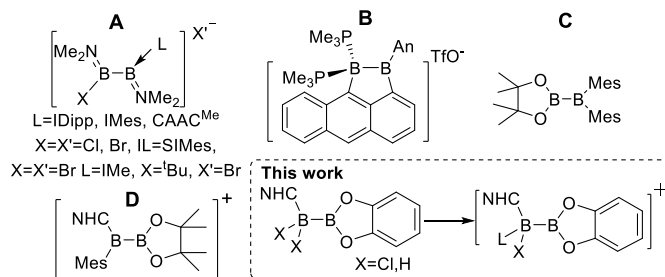

Figure 1. Structures of select previously reported unsymmetric electrophilic diboron (4) and diboron(5) compounds and inset, this work.

RESULTS AND DISCUSSION

Our previous work on the interaction of Lewis bases with diboron(4) compounds described the synthesis of the mono-NHC adduct $B_2cat_2(IMe)$ (IMe = tetramethylimidazol-2-ylidene).[12] The re-

action of B$_2$cat$_2$(IMe), **1-IMe**, with one equivalent of BCl$_3$ in toluene at room temperature results in the formation of the new sp^2-sp^3 NHC adduct **2-IMe**, which was isolated in 72% yield, with chlorocatecholborane observed as the side product (Scheme 1). The ^{11}B NMR spectrum of **2-IMe** reveals two resonances, one at 36.4 ppm (broad) for the sp^2-B center and one at –6.2 ppm (sharp) for the sp^3-B center. The same methodology was applied to synthesize the IMes and IDipp derivatives (**2-IMes** and **2-IDipp**, respectively, IMes = 1,3-dimesitylimidazol-2-ylidene, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in good yields (77 and 81%), with the ^{11}B NMR spectra of both compounds being very similar to that observed for **2-IMe**. It should be noted that analogous chemistry can be performed with BBr$_3$,[14] however, attempts using other boron Lewis acids such as BPh$_3$, B(C$_6$F$_5$)$_3$ or L-BH$_3$ resulted in either no reaction or produced intractable products with no analogues of **2-IMe** isolable.
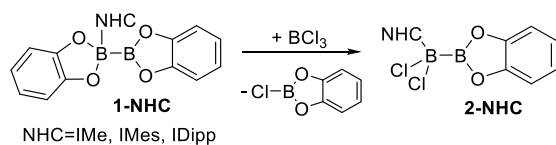
Scheme 1. Reaction of 1-NHC with BCl$_3$ to give 2-NHC.

Single crystals of **2-IMe** suitable for X-ray crystallography were obtained by dissolution in *ortho*-dichlorobenzene (*o*-DCB) and layering with pentane. This confirmed the formulation, with the structure containing one four-coordinate boron and one three-coordinate trigonal planar (angles sum to 359.7) boron center. The B-B bond length in **2-IMe** is in the range 1.683(8) to 1.699(8) Å (four inequivalent molecules of **2-IMe** are present in the asymmetric unit) which is slightly shorter than in compound **1-IMe** (1.729(3) Å) and B$_2$pin$_2$-NHC adducts reported previously (B$_2$pin-NHC adduct = 1.743(2) and 1.730(3) Å)[13]. The B-C distance (1.630(7) Å) does not differ significantly from its **1-IMe** precursor (1.647(2) Å) (Figure 2).

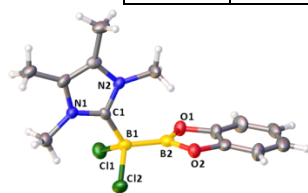|	sp^2-**B**(Cat)	**B**(IMe)	{BCat}^{a}
B$_2$cat$_2$	0.80	-	0.00
1-IMe	0.90	0.53	0.00
2-IMe	0.94	0.01	0.02
[3-IMe]$^+$	0.82	0.37	0.05

Figure 2. Solid state structure of **2-IMe**. Ellipsoids are shown at the 50% probability level. Selected bond lengths (in Å) and angles (in º): B1-B2 1.686(8), B1-C1 1.629(8), Cl1-B1-Cl2 108.3(3), Cl1-B1-C1 108.1(4), Cl2-B1-C1 105.3(4). Right, NBO charges calculated at the M06-2X/6-311G(d,p) level, a = {BCat} refers to the overall charge on the BCat unit containing the three-coordinate boron center.

Compound **2** may be formed by a process involving either (i) a B-B cleavage step, where transfer of a nucleophilic {BCat}$^−$ moiety from **1-NHC** to BCl$_3$ occurs followed by chloride transfer from [CatB-BCl$_3$]$^−$ to a [CatB(NHC)]$^+$ cation and subsequent NHC transfer; or, (ii) interaction of BCl$_3$ with the oxygen atom of a catechol group, leading to B-O / B-Cl substituent exchange, but no B-B cleavage. To obtain a feasible mechanism for the formation of **2-**

NHC, we performed a DFT study on the initial steps of the reaction. Calculations were carried out at the M06-2X/6-311G(d,p) level with a DCM polarizable continuum medium (PCM) solvation model. Despite extensive searching we were not able to locate any pathway involving the CatB-sp^2 unit reacting as a nucleophile to BCl$_3$ to form [CatBBCl$_3$]$^−$ and [CatB(NHC)]$^+$. Analysis of the charge distribution by NBO calculations (Figure 2, right) showed that in **1-IMe** the B sp^2 atom remains positively charged, meanwhile the B sp^3 atom gains electron density (relative to that in B$_2$Cat$_2$) and overall this is similar to the charge distribution calculated previously for B$_2$pin$_2$(IMes).[15] Notably, the overall charge on the entire sp^2-BCat unit is effectively zero in **1-IMe**, which is distinct to that found for alkoxide-activated diboron(4) compounds (where the sp^2 B(OR)$_2$ center is overall partially negatively charged). Thus as previously observed,[15] NHC activation of diboron compounds results in the formation of a less nucleophilic sp^2-B(OR)$_2$ group than that formed by activation with alkoxide.[15] For the second possible mechanism, Scheme 2 shows the calculated relative electronic and total energies of the different calculated intermediates for the first O/Cl exchange. Starting from compound **1-IMe**, coordination of BCl$_3$ to an oxygen atom of the two different catechol units gives two different intermediates **1a** and **1b**. The difference in electronic energy between them is 19.1 kcal/mol, with the more stable intermediate being that with BCl$_3$ coordinated to the catechol bound to the B-sp^3 center (**1a**), as expected. From this intermediate, a transfer of chloride from the BCl$_3$ unit to the boron center occurs through **TS$_{1a-1c}$** with a relatively low energy barrier of 4.6 kcal/mol. This results in the formation of intermediate **1c,** containing a ROBCl$_2$ moiety, which is slightly less stable than **1a**. From here, a second oxygen/chloride transfer would give compound **2-IMe** and CatBCl.
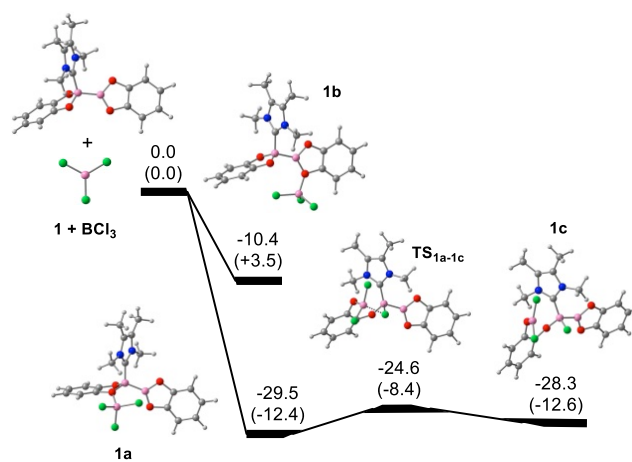
Scheme 2. Calculated energy profile for the possible initial steps of the B-O cleavage mechanism. Electronic and Gibbs free energies (in parenthesis) in kcal/mol.

Before investigating the synthesis of diboron(4) monocations derived from **2-NHC**, calculations were performed to probe the charge distribution (using the NBO model), frontier orbital energy and Lewis acidity. The change of catecholato for two chlorides decreases the positive charge on the B(IMe) center in **2-IMe** relative to **1-IMe**, consistent with a lower degree of B-Cl sigma bond polarization (charge on Cl = –0.3) relative to B-O (charge on O = –0.8). The polarization of the B-B bond is effectively unchanged on OR for Cl exchange as indicated by the overall charge on the entire {BCat} unit remaining effectively zero. In **[3-IMe]$^+$** the removal of chloride to generate the unit positive charge does not significantly alter the overall charge on the {BCat} unit. Instead, the unit positive charge is localized on the B-IMe moiety, despite the effectively co-planar arrangement of the C-B-Cl and O-B-O moieties. In the B-IMe unit the boron center carries the largest degree of positive

charge, as would be expected based on its more electropositive nature. The HOMOs for **2-IMe** and **[3-IMe]⁺** (figure 3) were found to be very similar in character while the LUMOs are slightly more distinct, with more boron character present in the LUMO of **[3-IMe]⁺**. As expected, the relative LUMO energies indicate that compound **2-IMe** is a weak Lewis acid while the diboron(4) monocation, **[3-IMe]⁺**, is a stronger Lewis acid. This is supported by calculation of the chloride-ion affinity (CIA) of **[3-IMe]⁺** relative to AlCl₃, which was estimated using an approach based on the energy change for the transfer of chloride from [AlCl₄]⁻ to the borenium cation (Figure 3, bottom). This value gives insight into the accessibility of the borenium cation by halide abstraction. The calculated CIA for **[3-IMe]⁺** is 12.3 kcal/mol (at the B-Cl(IMe) centre) relative to AlCl₃, which is comparable with previously synthesized borenium cations of type [(amine)BCl₂]⁺,[16] and thus indicates the feasibility of halide abstraction from **2-IMe** using Lewis acids such as AlCl₃.

$$[\text{3-IMe}]^+ \;+\; [\text{AlCl}_4]^- \;\xrightarrow{\;\Delta H_{CIA}=12.3\;\text{kcalmol}^{-1}\;}\; \text{2-IMe} \;+\; \text{AlCl}_3$$
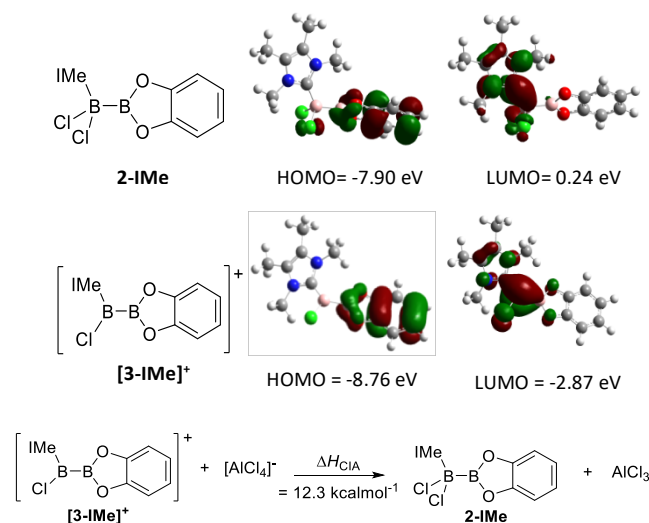
Figure 3. HOMO and LUMO representations for **2-IMe** and **[3-IMe]⁺** at an isosurface value of 0.04. Bottom, the relative (to AlCl₃) chloride ion affinity of **[3-IMe]⁺**.

Compound **2-IMe** was reacted with AlCl₃ using a range of conditions (temperature, solvent) and this led to the complete consumption of **2-IMe** and formation of [AlCl₄]⁻ (by multinuclear NMR spectroscopy). However, in the ¹¹B NMR spectrum, we were only able to identify BCl₃ (minor) and CatBCl (major) as products of this reaction. No intermediates were observed, and similar outcomes were achieved using other halide abstracting agents, e.g. K[B(C₆F₅)₄] and NaBArᶜˡ(BArᶜˡ₄ = [B(3,5-Cl₂-C₆H₃)₄]⁻) with Cat-BCl observed formed on reaction of **2-IMe** with each of these salts. The formation of CatBCl from **2-IMe**/AlCl₃ also occurs in chlorobenzene, indicating that the halide in CatBCl is unlikely to derive from the solvent. The results of the reaction of **2-IMes** and **2-IDIPP** with AlCl₃ and K[B(C₆F₅)₄] did not lead to any identifiable or isolable species in our hands.

Attempts to trap the putative cation **[3-IMe]⁺** by performing halide abstraction in the presence of a range of small molecules (e.g. H₂, CO, terminal and internal alkynes) still produced CatBCl along with other intractable products. Therefore, attempts to trap the putative cation by adding better nucleophiles, specifically phosphine and amine Lewis bases, were explored. It should be noted that **2-IMe** shows no reaction with the phosphines and amines used in this study in the absence of exogenous Lewis acid (by multinuclear NMR spectroscopy), consistent with the low Lewis acidity of **2-IMe** indicated by calculations. The reaction of **2-IMe** with AlCl₃ in the presence of one equivalent of PPh₃ results in the formation of the Lewis base-stabilized diboron(5)-monocation **4** (Figure 4). The ¹¹B NMR spectrum of **4** shows two resonances, one for the sp² boron atom at 37.7 ppm and one for the sp³ boron atom at –14.8

ppm. The ³¹P{¹H} NMR spectrum of **4** shows one broad signal at 1.44 ppm. The structure of **4** was confirmed by X-ray diffraction (Figure 4b) which confirmed the presence of an sp³ B and an sp² B center. The B-B bond length in **4** was 1.717(8) Å, which is longer than that in **2-IMe** but shorter than Wang's diboron(5) (1.754(11) Å) monocation (PinB-B(NHC)(4-DMAP)Mes, the 4-DMAP adduct of compound **D**).[10] The P-B distance in **4** (1.970(6) Å) is consistent with that found in other phosphine-containing boronium cations.[11b] The addition of a second equivalent of AlCl₃ to **4** did not abstract the second chloride, with resonances for the cationic portion of **4** unchanged.

When **2-IMe** was treated with one equivalent of 2-DMAP and one equivalent of K[B(C₆F₅)₄] in o-DCB, the ¹¹B NMR spectrum of the reaction mixture indicated conversion to a new boron-containing product containing both sp² and sp³ boron centers, δ_{11B} = 29.9 and –3.7 ppm, respectively. Crystals were isolated from the reaction mixture after layering with pentane. The structure of **5** confirms the formation of a diboron monocation of formula [CatB-B(IMe)Cl(2-DMAP)][B(C₆F₅)₄]. While the B-B distance of 1.711(5) Å is very similar to that in **4**, the presence of the pendant NMe₂ group has a noticeable structural effect. The NMe₂ group of 2-DMAP is orientated towards the boron center of the BCat moiety with a B-N distance of 2.056 Å, suggesting a weak interaction between the NMe₂ group and the sp²-B center. Consistent with a weak interaction between N and B is the small deviation from planarity of the BCat moiety (sum of angles = 354.3°). The distinct δ_{11B} chemical shift of the sp² B centre in **5** relative to **4** (29.9 and 37.7 ppm, respectively) suggests that this interaction persists in solution.
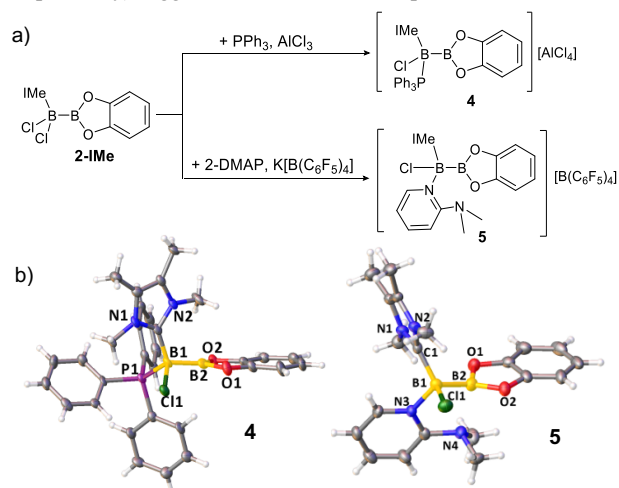

Figure 4. a) Synthesis of diboron-monocations **4** and **5**. b) X-Ray crystal structures of **4** and **5**. Selected bond lengths in Å: **4**: B1-B2 1.717(8), B1-C1 1.621(7), B1-P1 1.970(6); **5**: B1-B2 1.711(5), B1-C1 1.629(4), B1-N3 1.600(4).

Attempts to abstract the remaining chloride from **5** upon addition of K[B(C₆F₅)₄] or by reacting **2-IMe** with 2-DMAP and excess AlCl₃ failed (with **5** persisting by multinuclear NMR spectroscopy). The relative (to AlCl₃) chloride ion affinity of the putative diboron(4) dication derived from chloride abstraction from **5** (and before binding of NMe₂, Scheme 3) was calculated and found to be –1.2 kcal/mol, consistent with the lack of chloride abstraction using AlCl₃. The LUMO energy of compound **5** (–1.93 eV) is much higher than for **[3-IMe]⁺**, suggesting it is a weaker Lewis acid, and consistent with this, compound **5** did not react with alkynes such as 3-hexyne.
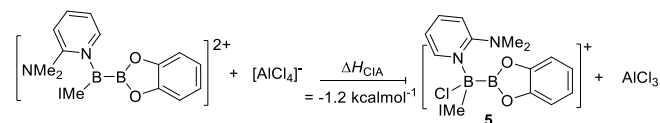
Scheme 3: The CIA of the dication derived from **5**

Due to the instability of putative **[3-IMe]⁺**, our next target was exchanging a chloride group for an alternative substituent that is also amenable to abstraction using common reagents, specifically the 1,1-dihydrodiboron congener of **2-IMe**. While reaction of **2-IMe** with silanes such as HSiEt₃ or HSiPh₃ gave complex mixtures of products that were intractable in our hands, the reaction of **2-IMe** with 10 mol% of Na[BAr$^{Cl}_4$] and two equivalents of Bu₃SnH resulted in the rapid formation of the 1,1-dihydrodiboron derivative CatB-B(H)₂IMe, **6-IMe**, within minutes. The ¹¹B NMR spectrum of the reaction mixture containing **6-IMe** shows a broad signal at 42.9 ppm corresponding to the sp²-B and a broad singlet at –40.1 ppm corresponding to the dihydroborane (Figure 5), which is similar to similar compounds reported previously.[17] Presumably, halide abstraction to form the **[3-IMe]⁺** cation facilitates hydride transfer from Bu₃SnH, as in the absence of NaBAr$^{Cl}_4$ the reaction is extremely slow and yields multiple products. Bu₃Sn-Cl is observed as the expected tin byproduct from this reaction (and the ¹¹B resonance for [BAr$^{Cl}_4$] persists). In the reaction mixture, compound **6-IMe** proved to be thermally sensitive, with the ¹¹B NMR spectrum after 5 min at room temperature showing some decomposition, as indicated by the appearance of a quartet at –36.6 ppm ($J = 84.1$ Hz) that corresponds to BH₃-IMe.[18] The other product(s) that must form alongside IMe-BH₃ proved intractable and were not able to be identified in our hands. The purification of compound **6-IMe** from M[BAr$^{Cl}_4$] (M = ?), Bu₃SnCl and the decomposition products was also not successful in our hands.

The accessibility of the cation derived from **6-IMe** initially was explored by calculation of the hydride ion affinity of **[7-IMe]⁺**, which was found to be –52.7 kcal/mol relative to BEt₃ (Figure 5, top).[16] This suggests that the putative **[7-IMe]⁺** is less Lewis acidic toward hydride than Ph₃C⁺ but more so than B(C₆F₅)₃.[19] The hydride ion affinity of **7-IMe** is in fact comparable to other borenium cations (e.g. E, –47.8 kcal/mol).[16] Inspection of the frontier molecular orbitals revealed that the LUMO of **[7-IMe]⁺** was found to be lower in energy than its precursor (**6-IMe** –0.39 eV; **[7-IMe]⁺** – 2.63 eV) and was mainly located on the B-IMe group. In contrast, the LUMO of **6-IMe** was located mainly on the Bcat moiety. The LUMOs of the two cations **[7-IMe]⁺** and **[3-IMe]⁺** are similar in both character and energy.

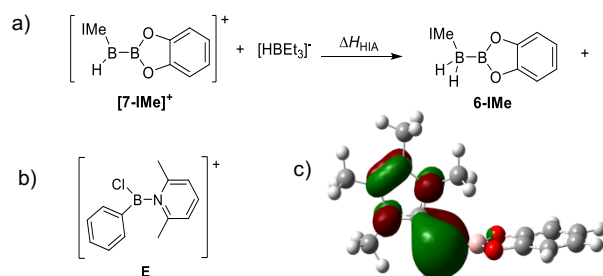**Figure 5. a) Isodesmic reaction used to calculate HIA. b) Borenium cation E that possesses a similar HIA. c) LUMO representation of [7-IMe]⁺ (isosurface value of 0.04).**

Attempts were made to form **[7-IMe]⁺** directly from the crude reaction mixture derived from **2-IMe** / M[BAr$^{Cl}_4$] / Bu₃SnH. The addition of trityl salts to this reaction mixture in haloarene solvents resulted in formation of Ph₃CH, however the only identifiable new boron containing species was CatBH. CatBH is not derived from solvent activation, as CatBH is also formed when hydride abstraction is repeated in d₅-bromobenzene, therefore the decomposition pathway of putative **[7-IMe]⁺**, which forms CatBH (and unidentified by-products), appears to be comparable to that for **[3-IMe]⁺** which forms CatBCl and unidentified by-products. Seeking to trap the putative **[7-IMe]⁺** using competent nucleophiles, the mixture containing **6-IMe** (< 2 minutes after its formation) was reacted with a number of phosphine / B(C₆F₅)₃ frustrated Lewis pairs. The addition of P^{t}Bu₃ and B(C₆F₅)₃ gave the best result, producing a single major new boron compound with its ¹¹B NMR spectrum showing a

resonance at 39.2 ppm attributed to the B of the BCat moiety, one at –37.2 attributed to the BH and one doublet at –25.8 ppm which is consistent with HB(C₆F₅)₃. However, the ³¹P{¹H} NMR spectrum revealed several products and we were not able to isolate any of the desired unsymmetrical diboron(5) cations derived from **6-IMe** despite multiple attempts.

In order to increase the stability of the B-H diboron species, IMe was replaced with IMes and IDipp. Using the same procedure (addition of 10 mol% of Na[BAr$^{Cl}_4$] and two equivalents of Bu₃SnH), we were able to synthesize the corresponding 1,1-dihydro-diboron(5) compound for both NHCs, termed **6-IMes** and **6-IDipp**. However, the isolation of **6-IMes** and **6-IDipp** was not possible to achieve since Na[BAr$^{Cl}_4$] co-crystallized with both species and could not be separated in our hands. Nevertheless, the ¹¹B NMR spectrum of **6-IMes** shows similar resonances to that observed for **6-IMe**, including a broad signal at 42.4 ppm and a broad signal at –40.0 ppm, which supports the formation of **6-IMes**. The solid-state structure of compound **6-IMes**, crystallized by slow evaporation of a saturated solution in DCM, further confirmed the formulation of this series of compounds (Figure 6). The B-B bond distance in **6-IMes** at 1.686(4) Å is slightly shorter than those displayed by Braunschweig et al. (1.702(6) Å) for a related dihydro-diboron(5) but comparable to the B-B distance in **2-IMe**.[13] In all these compounds, the B-H coupling is not clearly resolved, which was also the case for other 1,1-dihydroboranes.[17]
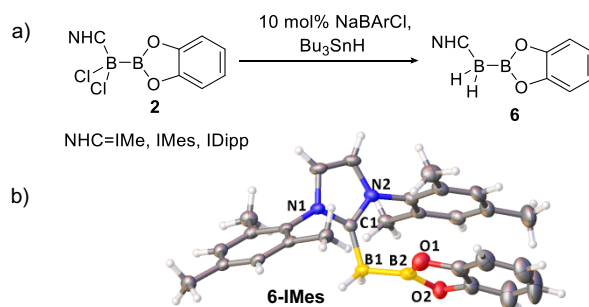

Figure 6. a) Synthesis of 1,1-dihydrodiboron(5) compounds b) Solid state structure of **6-IMe**, ellipsoids at 50% probability. Selected bond lengths in Å: B1-B2 1.686(4), B1-C1 1.605(3).

Compounds **6-IMes** and **6-IDIPP** proved to be more thermally stable in solution, and formation of the hydrodiboron monocations **[7-NHC]⁺** was explored. The reaction of **6-IMes** or **6-IDIPP** (containing Na[BAr$^{Cl}_4$] impurity) with [Ph₃C][B(C₆F₅)₄] again led to decomposition, with CatBH again observed at 27.8 ppm ($J = 210$ Hz) as one of the products in the ¹¹B NMR spectrum. Attempts to form a Lewis base-stabilized hydrodiboron(4) monocation with these compounds using phosphine/B(C₆F₅)₃ FLPs gave complex mixtures that proved intractable in our hands. Attempts to assess the reactivity of the putative cations **[7-NHC]⁺** by performing hydride abstraction from **6-NHC** in the presence of alkynes also led to complex mixtures.

The decomposition of the putative diboron(4) cations to form CatBCl and CatBH appears to be a common reaction pathway. The disparity between the stability of **[3-NHC]⁺** / **[7-NHC]⁺** and Wang's closely related compound **C** is noteworthy and is presumably due to the superior π donor properties of pinacol versus catechol, and the greater steric bulk of the Mes group (relative to H or Cl). However, it should be noted that with compound **C**, related B-B bond cleavage reactions occur, leading to the formation of MesBPin (Scheme 4, bottom).
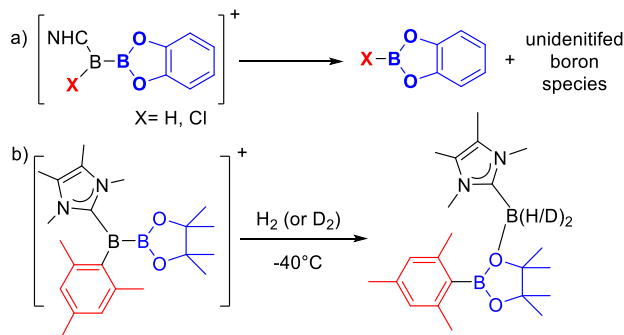
Scheme 4. a) Possible reaction pathway for the decomposition of [3-NHC]⁺ and [7-NHC]⁺. b) Reaction of Wang's borylborenium with H₂ or D₂.

CONCLUSIONS

In this work we have reported the synthesis of NHC-coordinated diboron compounds **2-NHC**. When the IMe congener of these diboron(5) compounds was treated with a Lewis base and AlCl₃ or K[B(C₆F₅)₄], formation of Lewis base-stabilized di-boron(5) monocations proceeded. However, in the absence of competent nucleophiles, the putative diboron(4) monocation [CatB-B(NHC)Cl]⁺ reacted to form CatBCl and other unidentified boron containing species. The reaction of **2-NHC** with 10 mol% of Na[BArᶜˡ₄] and two equivalents of Bu₃SnH provides access to a series of 1,1-dihydrodiboron (5) compounds. However, it was not possible to achieve the synthesis and isolation of the putative **[7-IMe]⁺** cation derived from hydride abstraction due to its instability, with CatBH observed to form rapidly. Thus, there appears to be a minimum steric and electronic stabilization requirement to afford access to diboron(4) monocations.

EXPERIMENTAL SECTION

All appropriate manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O₂ / H₂O levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents and amines were distilled from NaK, CaH₂, or K and degassed prior to use. Unless otherwise stated all compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII-400 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual protio impurities in the NMR solvents for ¹H and ¹³C{¹H} respectively, while ¹¹B,¹⁹F, ³¹P, ²⁷Al shifts are referenced relative to external BF₃-Et₂O, hexafluorobenzene, 85% phosphoric acid and Al(NO₃)₃ in D₂O (Al(D₂O)₆³⁺), respectively. Coupling constants J are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicities of the signals are indicated as "s", "d", "t" "q" "pent", "sept" or "m" for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively. Unless otherwise stated all NMR spectra are recorded at 293 K. Carbon atoms directly bonded to boron are not always observed in the ¹³C{¹H} NMR spectra due to quadrupolar relaxation leading to signal broadening. All calculations were conducted at the M06-2X/6-311G(d,p) level with a solvation model (PCM, CH₂Cl₂) using the Gaussian software package.[20] All geometry optimizations were full, with no restrictions. All stationary points located in the potential energy hypersurface were characterized as minima or transition states by vibrational analysis. Transition states had one and only one imaginary frequency, whose normal mode corresponded to the expected motion.

CatBBCl₂IMe (2-IMe). BCl₃ 1M in hexanes (2.42 mmol, 2.42 mL) was added to a stirred solution of B₂cat₂IMe (**1-IMe**) (2.42 mmol, 876 mg) in 20 mL of toluene at −77 °C. After the addition, the reaction mixture was warmed to room temperature and was stirred for 2 h. Afterwards, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid (786 mg, 72%). Elemental analysis calc.: C₁₃H₁₆B₂Cl₂N₂O₂: C, 48.07; H, 4.97; N, 8.62.

Found: C, 48.23; H, 4.82; N, 8.51. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.27 (m, 2H), 7.08 (m, 2H), 3.73 (s, 6H), 2.16 (s, 6H). ¹¹B NMR (128 MHz, CD₂Cl₂) δ = 36.4 (br s), −6.2 (br s). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ = 149.0, 126.5, 122.8, 112.9, 34.3, 9.3.

CatBBCl₂IMes (2-IMes) BCl₃ 1M in hexanes (0.92 mmol, 0.92 mL) was added to a stirred solution of B₂cat₂IMes (**1-IMes**) (0.92 mmol, 500 mg) in 20 mL of hexane and 5 mL of toluene at −77 °C. After the addition, the reaction mixture was warmed to room temperature and stirred for 2 h. Afterwards, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid (356 mg, 77%). Elemental analysis calc.: C₃₉H₄₄B₂N₂O₄: C, 64.21; H, 5.59; N, 5.55. Found: C, 64.02; H, 5.59; N, 5.73. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.10 (s, 2H), 7.00 (m, 2H), 6.94 (m, 2H), 6.79 (m, 4H), 2.19 (s, 12H), 2.09 (m, 6H). ¹¹B NMR (128 MHz, CD₂Cl₂) δ = 36.3 (br s), −6.3 (br s). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ = 149.2, 141.0, 136.1, 133.3, 129.5, 128.9, 124.2, 122.2, 112.2, 21.3, 18.5.

CatBBCl₂IDipp (2-IDIPP). BCl₃ 1M in hexanes (0.80 mmol, 0.80 mL) was added to a stirred solution of B₂cat₂IDipp (**1-IDIPP**) (0.80 mmol, 500 mg) in 20 mL of hexane and 5 mL of toluene at −77 °C. After the addition, the reaction mixture was warmed to room temperature and stirred for 2 h. Afterwards, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid (384 mg, 81%). Elemental analysis calc.: C₃₃H₄₀B₂Cl₂N₂O₂: C, 67.27; H, 6.84; N, 4.75. Found: C, 67.01; H, 6.87; N, 5.04. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.16 (m, 8H), 6.90 (s, 4H), 2.76 (sept, J = 7.0 Hz, 4H), 1.45 (d, J = 6.7 Hz, 12H), 1.11 (d, J = 6.8 Hz, 12H). ¹¹B NMR (128 MHz, CD₂Cl₂) δ = 36.6 (br s), −6.3 (br s). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ = 149.1, 146.6, 133.4, 131.3, 125.2, 124.2, 121.8, 112.3, 29.8, 26.3, 22.3.

[CatBBClIMe(PPh₃)][AlCl₄](4). PPh₃ (0.15 mmol, 39 mg) was added to a stirred solution of catBBCl₂IMe (**2-IMe**) (0.15 mmol, 49 mg) in 1 mL of o-dcb. After stirring the solution for 30 min, AlCl₃ (0.15 mmol, 20 mg) was added and the reaction mixture was stirred for 3 h. Afterwards, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid (96 mg, 89%). Elemental analysis calc.: C₃₁H₃₁AlB₂Cl₅N₂O₂: C, 51.68; H, 4.34; N, 3.89. Found: C, 51.33; H, 4.45; N, 4.01. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.73-7.63 (m, 10H), 7.60-7.55 (m, 5H), 7.22 (m, 2H), 7.13 (m, 2H), 2.93 (s, 6H), 2.17 (s, 6H). ¹¹B NMR (128 MHz, CD₂Cl₂) δ = 37.7 (br s), −14.8 (br s). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ = 148.1, 134.8 (d, J = 8.7 Hz), 133.9 (d, J = 2.7 Hz), 130.3 (d, J = 10.8 Hz), 129.7, 123.8, 123.6, 122.9, 113.3, 34.7, 9.9. ³¹P NMR (162 MHz, CD₂Cl₂) δ 1.44. ²⁷Al NMR (104 MHz, CD₂Cl₂) δ 103.8.

[CatBBCl(IMe)2-DMAP][B(C₆F₅)₄](5). 2-DMAP (0.15 mmol, 19 µL) was added to a stirred solution of catBBCl₂IMe (**2-IMe**) (0.15 mmol, 49 mg) in 1 mL of o-dcb. After stirring the solution for 30 min, K[B(C₆F₅)₄] (0.15 mmol, 164 mg) was added and the reaction mixture was stirred overnight. Afterwards, the reaction mixture was filtered and all volatiles were removed in vacuo. The residue was washed with pentane and benzene to yield a yellow solid (120 mg, 73%). Elemental analysis calc.: C₄₄H₂₆B₃ClF₂₀N₂O₂: C, 48.46; H, 2.40; N, 5.14. Found: C, 48.17; H, 2.41; N, 5.10. ¹H NMR (400 MHz, CD₂Cl₂) δ = 8.75 (d, J = 6.1, 1H), 8.39 (dd, J = 7.6, 7.5 Hz, 1H), 7.74 (m, 2H), 7.09 (m, 2H), 6.98 (m, 2H), 3.44 (s, 6H), 2.60 (s, 6H), 2.18 (s, 6H). ¹¹B NMR (128 MHz, CD₂Cl₂) δ = 29.9 (br s), −3.7 (br s), −16.7 (sharp, B(C₆F₅)₄). ¹³C{¹H} NMR (101MHz, CD₂Cl₂) δ = 163.2, 149.5, 148.7 (d, J = 240 Hz) 147.4, 147.3, 138.8 (d, J = 245 Hz), 136.9 (d, J = 245 Hz), 128.4, 125.7, 122.4, 121.7, 112.1, 46.2, 34.4, 9.4. ¹⁹F NMR (376 MHz, CD₂Cl₂) δ −132.1 to −134.6 (m), −163.5 (t, J = 20.3 Hz), −167.1 to −169.6 (m).

CatBBH₂(IMes) (6-IMes). Bu₃SnH (0.80 mmol, 0.215 mL) was added to a stirred solution of catBBCl₂IMes (**2-IMes**) (0.40 mmol, 200 mg) and Na[BArᶜˡ] (0.04 mmol, 25 mg) in 10 mL of DCM. After stirring the solution for 1 h, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid (132 mg, 76%). An analytically pure sample of **6-IMes** could not be obtained as during purification Na[BArᶜˡ₄] was co-crystallized with **6-IMes** and could not be separated. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.03 (s, 2H), 6.95 (m, 2H), 6.93 (s, 4H), 6.88 (m, 2H), 2.27 (s, 6H), 2.10 (s, 12H). ¹¹B NMR (128MHz, CD₂Cl₂) δ = 42.4 (br s), -40.0 (br s). ¹³C{¹H} NMR (101MHz, CD₂Cl₂) δ = 149.5, 139.7, 135.7, 135.0, 129.5, 121.5, 121.3, 111.5, 21.4, 18.0.

CatBBH₂IDipp (6-IDIPP). Bu₃SnH (0.68 mmol, 0.183 mL) was added to a stirred solution of catBBCl₂IDipp (**2-IDIPP**) (0.34 mmol, 200 mg) and NaBArCl (0.034 mmol, 21 mg) in 10 mL of DCM. After stirring the solution for 1 h, all volatiles were removed in vacuo. The residue was washed three times with pentane to yield a white solid. (106 mg, 60%). An analytically pure sample of **6-IMes** could not be obtained as during purification Na[BAr$^{Cl}_4$] was co-crystallized with **6-IMes** and could not be separated. ^{1}H NMR (400 MHz, CD₂Cl₂) δ = 7.43 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 7.8 Hz, 4H), 6.93 (m, 2H), 6.86 (m, 2H), 2.73 (sept, J = 6.8 Hz, 4H), 1.18 (d, J = 6.9 Hz, 12 H), 1.15 (d, J = 6.9 Hz, 12 H). ^{11}B NMR (128 MHz, CD₂Cl₂) δ = 42.5 (br s), –39.3 (br s). ^{13}C{^{1}H} NMR (101 MHz, CD₂Cl₂) δ = 149.62, 146.34, 134.97, 130.55, 124.51, 122.87, 121.35, 111.66, 29.21, 25.75, 23.01.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional experimental details and NMR spectra (PDF)
Coordinates for all calculations (XYZ)
Crystallographic data (CCDC 1840161, 1840162, 1840163, 1840193) (CIF)

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