Boron–Carbene Adducts

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# Planar N-Heterocyclic Carbene Diarylborenium Ions: Synthesis by Cationic Borylation and Reactivity with Lewis Bases**

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*In memory of Yves Chauvin*

***Abstract:*** *The NHC–borane adduct (IBn)$BH_3$ (**1**) (NHC = N-heterocyclic carbene; IBn = 1,3-dibenzylimidazol-2-ylidene) reacts with $[Ph_3C][B(C_6F_5)_4]$ through sequential hydride abstraction and dehydrogenative cationic borylation(s) to give singly or doubly ring closed NHC–borenium salts **2** and **3**. The planar doubly ring closed product $[C_3H_2(NCH_2C_6H_4)_2B][B(C_6F_5)_4]$ is resistant to quaternization at boron by $Et_2O$ coordination, but forms classical Lewis acid–base adducts with the stronger donors $Ph_3P$, $Et_3PO$, or 1,4-diazabicyclo[2.2.2]octane (DABCO). Treatment of **3** with $tBu_3P$ selectively yields the unusual oligomeric borenium salt trans-$[(C_3H_2(NCH_2C_6H_4)_2B)_2(C_3H_2(NCHC_6H_4)_2B)][B(C_6F_5)_4]$ (**7**).*

Three-coordinate boron compounds are considered as quintessential Lewis acids. Although thoroughly established as cornerstones of Lewis acid/base organic chemistry and catalysis,[1] boranes continue to be investigated in search of new reactivity. Specifically, highly electrophilic boron species have drawn attention for their reactivity with small molecules, such as $H_2$ and silanes.[2] We, and others, have exploited pairings of bulky Lewis acids and bases, sometimes dubbed frustrated Lewis pairs (FLPs), to uncover the ability of main-group reagents to activate a wide variety of small molecules.[3]

Three-coordinate boron cations, known as borenium ions,[4] are a relatively underexplored class of highly electrophilic boron-containing Lewis acids. Nevertheless such species have fostered interest for an array of C–B bond-forming reactions[5] and catalytic processes[6] while Yamaguchi and co-workers have explored the photophysical properties of a planar *B*-phenylborataanthracene anion.[7] We have shown that an NHC–borenium salt, $[(IiPr)BC_8H_{14}][B(C_6F_5)_4]$ (IiPr = 1,3-di-*iso*-propylimidazol-2-ylidene), acts as an effective metal-free catalyst for the hydrogenation of imines and enamines[8] by an FLP-type mechanism. More recent work on this catalysis has revealed that sterically demanding NHCs have a deleterious effect on activity.[9] Although steric protection is typically key to the FLP-type reactivity of highly electrophilic boranes, this trend in activity prompted us to consider alternative approaches to the design of NHC–borenium ions for use in FLP chemistry.

Planar constrained di- and triarylboranes have been explored using a number of synthetic approaches.[10] In addition to remarkable effects on electronic and photochemical properties, enforced planarity with adjacent aryl groups often stabilizes three-coordinate boranes towards donor-mediated decomposition pathways.[10f,i] This stabilization functions by inhibiting pyramidalization of the boron center and does not necessitate its steric protection. Encouraged to investigate planar constrained NHC–(aryl)borenium ions, we approached their syntheses noting the recent emergence of cationic borylation as a facile route to C–B bond formation. For example, Vedejs and co-workers have shown that highly selective dehydrogenative borylation of neighboring aryl and alkyl groups can be effected by amine-stabilized hydrido–borenium ions.[5b,c,k] Moreover, Hatakeyama et al. have prepared neutral BN-fused twisted polycyclic aromatic compounds using related tandem Friedel–Crafts-like electrophilic borylations.[10e]

Herein, we investigate facile NHC-directed dehydrogenative cationic borylation reactions to provide a synthetic route to planar diarylborenium ions. The reactivity of a resulting planar borenium cation with Lewis bases is probed. Although the boron center of this cation is not strongly coordinated by $Et_2O$, classical Lewis acid–base adducts can be formed with $Ph_3P$, $Et_3PO$, or 1,4-diazabicyclo[2.2.2]octane (DABCO). Divergent reactivity is observed with the sterically demanding base $tBu_3P$, where reaction affords an unusual salt in which the cation contains three boron centers.

The NHC–borane adduct **1** was readily prepared in 56% yield from the reaction of in situ generated 1,3-dibenzylimidazol-2-ylidene (IBn) with $Me_3NBH_3$. This is directly analogous to NHC–borane syntheses described by Brahmi et al.[11] An X-ray crystallographic study of **1** confirmed the formulation of this compound as (IBn)$BH_3$ and revealed an average $B–C_{NHC}$ bond length of 1.599(4) Å over two molecules of **1** in the unit cell (see the Supporting Information). Treatment of **1** with a stoichiometric amount of $[Ph_3C][B(C_6F_5)_4]$ in $C_6D_5Br$ at room temperature results in the quantitative formation of **2** and triphenylmethane with concomitant loss of hydrogen gas (Scheme 1). In the $^{11}B$ NMR spectrum, resonance signals appeared at $\delta = 48.6$ and $-16.7$ ppm and $^1H$ NMR data were consistent with the formulation of **2** as $[(C_3H_2NBn(NCH_2C_6H_4)BH][B(C_6F_5)_4]$.

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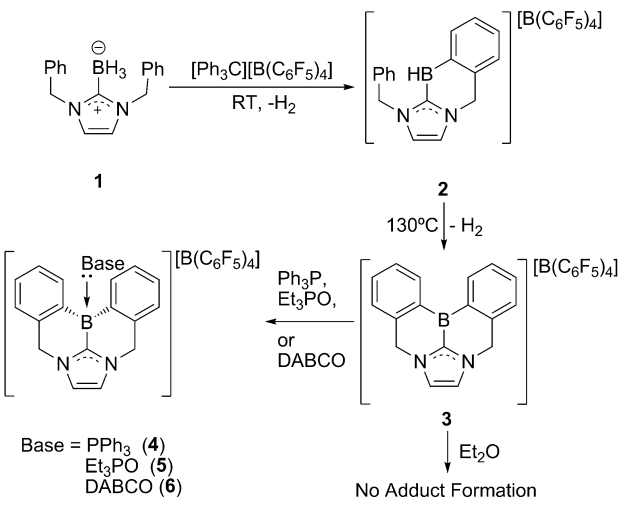



***Scheme 1.*** Synthesis of **3** and its reactivity with Lewis bases $Et_2O$, $PPh_3$, $Et_3PO$, and DABCO.

From a larger scale synthesis, **2** could be isolated by crystallization in 50% yield. An X-ray crystallography study confirmed the structure of **2** as a planar borenium salt bearing one *ortho*-borylated benzylic arene ring.[18] The B–$C_{NHC}$ bond length is contracted to 1.544(4) Å with a B–$C_{aryl}$ bond length of 1.536(3) Å (Figure 1a). Although NMR data are consistent with a three-coordinate cationic boron center in **2**, close contact is observed between this atom and the chloride of the solvate $C_6H_5Cl$ in the solid state.

Further dehydrogenative borylation of **2** occurred at 130 °C in $C_6D_5Br$ leading to complete conversion into the new species **3** after 28 h (Scheme 1). The resonance signals in the $^{11}B$ NMR spectrum at $\delta = 42.4$ and $-16.6$ ppm together with corroborating $^1H$ NMR spectroscopic data, in particular the single resonance attributable to the benzylic groups, support the formulation of **3** as $[C_3H_2N_2(CH_2C_6H_4)_2B][B(C_6F_5)_4]$. This compound was isolated in a larger scale reaction starting from **1** in 84% yield. The formulation of **3** as a doubly arylated

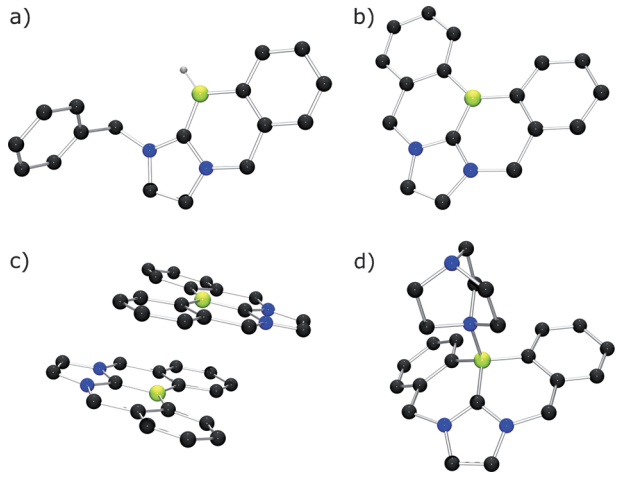



***Figure 1.*** POV-ray depictions of cations of a) **2** and b) **3** and head-to-tail stacked dimers of c) **3** and d) **6**. Hydrogen atoms, with the exception of B*H*, are omitted for clarity. Atom colors: C = black; H = gray; N = blue; B = yellow.

NHC–borenium salt was confirmed by a X-ray crystallography (Figure 1b).[18] A B–$C_{NHC}$ bond length of 1.538(3) Å was observed. Interestingly, the sterically unprotected cation of **3** does not show close contact to the $[B(C_6F_5)_4]$ counterion in the solid state. Rather, cations of **3** form head-to-tail π-stacked dimers with a closest approach of 3.4 Å (Figure 1c). This is reminiscent of neutral 10a-aza-10b-borapyrene prepared by Piers and co-workers.[12] The cation is planar about the boron center with sums of B–C bond angles equal to 360°. The $C_{NHC}$-B-C bond angles (112.6(2)° and 112.0(2)°) in the cation are less than the idealized 120° because of their incorporation into azaboracycles. It is noteworthy that the cation of **3** possesses markedly shorter B–C bond lengths and an upfield shifted signal in the $^{11}B$ NMR spectrum compared to the non-constrained NHC–diarylborenium salt $[(IMe)BMes_2][OSO_2CF_3]$ described by Matsumoto and Gabbaï.[13] These observations echo similar bond-length contractions and upfield shifts of signals in the $^{11}B$ NMR spectrum shown by Yamaguchi and co-workers[10f] for planar constrained arylboranes relative to analogous non-constrained arylboranes.

Addition of the donors $PPh_3$, $Et_3PO$, or DABCO to **3** results in the quaternization of the cationic boron center to afford the corresponding adducts (with $PPh_3$ as donor to form **4**, $Et_3PO$ to form **5**, and DABCO to form **6**; Scheme 1). The coordination of $Et_3PO$ to **3** provides the basis for assessment of the Lewis acidity of the borenium cation in **3** by the Gutmann–Beckett method.[14] Relative to free $Et_3PO$, the downfield shift of the signal in the $^{31}P\{^1H\}$ NMR spectrum of **5** detected at $\delta = 79.1$ ppm in $CD_2Cl_2$ ($\Delta\delta = 28.9$ ppm) suggests that the cation of **3** is slightly more Lewis acidic than the strongly acidic $B(C_6F_5)_3$ ($\Delta\delta = 26.7$ ppm). However, **3** is apparently less acidic than the borenium ion $[(C_6H_4O_2)B(NEt_3)]^+$ prepared by Ingleson and co-workers, whose adduct with $Et_3PO$ gives rise to a signal in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 88.3$ ppm.[15] The product **6**, isolated in 96% yield, exhibited resonance signals in its $^{11}B$ NMR spectrum at $\delta = -7.5$ ppm and $-16.6$ ppm corresponding to the four-coordinate cation and anion, respectively. The $^1H$ NMR spectrum of **6** shows inequivalent benzylic protons resulting from adduct formation. X-ray structural data (Figure 1d) revealed a B–N bond length of 1.684(3) Å with the sum of B–C bond angles about boron decreased to 329.3°.

The generation of compounds **4** to **6** demonstrates the ability of **3** to form classical Lewis acid–base adducts. This is indeed consistent with the steric accessibility of the cation of **3**. Nevertheless, treatment of **3** with a 14.5-fold excess of $Et_2O$ in $CD_2Cl_2$ results in the appearance of a broad signal at $\delta =$ 19.1 ppm in the $^{11}B$ NMR spectrum for the cationic boron center and a single equivalent $^1H$ NMR resonance corresponding to benzylic protons. These data suggest a three-coordinate environment at the cationic boron center. The upfield shift of the $^{11}B$ NMR resonance signal with respect to **3** likely indicates a weak interaction of $Et_2O$ with the cationic boron center. This resistance to pyramidalization stands in contrast to other strong boron-centered Lewis acids, including $B(C_6F_5)_3$, which readily form $Et_2O$ adducts. Nevertheless, this result echoes the donor stability reported for planar constrained triarylboranes.[10f]

Upon treatment of **3** with the sterically encumbered Lewis base $t$Bu$_3$P, NMR spectroscopy did not indicate the formation of an adduct. Instead, two equivalents of $t$Bu$_3$P were converted into the known cation $[t\text{Bu}_3\text{PH}]^+$ for every three equivalents of **3** suggesting some degree of oligomerization. The nature of the boron-containing product **7** was elucidated by X-ray crystallography.[18] The structure of **7** results from the net twofold deprotonation of a single cation of **3** at each of the benzylic positions followed by coordination of these carbons to the boron of two cations of **3** to give a *trans* $C_2$-symmetric borenium salt (Figure 2; Scheme 2). The newly formed C–B bonds are 1.716(3) Å and 1.717(3) Å in length giving a pseudo-tetrahedral geometry about the neutral four-coordinate boron centers. Presumably the *trans* geometry of the

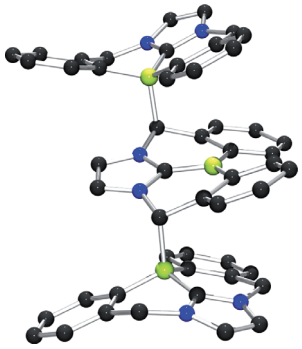
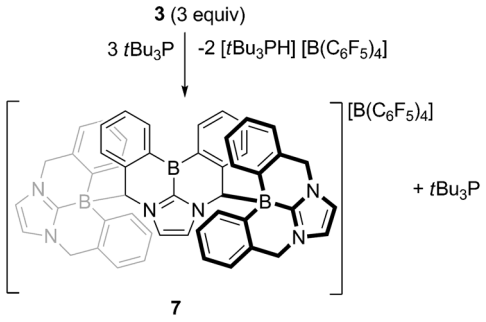


***Figure 2.*** POV-ray depiction of the cation of **7**. Hydrogen atoms are omitted for clarity. Atom colors: C = black; H = gray; N = blue; B = yellow.




***Scheme 2.*** Synthesis of **7**.

B substituents appended to the benzylic carbons is sterically favored over the *cis* arrangement. As expected the B–$C_{NHC}$ and B–$C_{aryl}$ bond lengths of these boron centers are elongated with respect to **3**. The central cationic boron center retains planarity with a sum of B-C bond angles equal to 360°. The B–$C_{NHC}$ bond length of 1.525(3) Å and the B–$C_{aryl}$ bond lengths of 1.539(3) Å and 1.542(3) Å of the cationic boron center are contracted with respect to **3**. Efforts to re-dissolve crystals of **7** were unsuccessful. Nonetheless, monitoring the initial reaction by $^1$H NMR spectroscopy and HRMS provided data consistent with the near-quantitative generation of **7** after four hours. In the $^{11}$B NMR spectrum, two resonance signals are detected for **7** at $\delta = -14.6$ and $-16.6$ ppm, corresponding to the neutral four-coordinate B centers and $[B(C_6F_5)_4]^-$, respectively, whereas the central boron atom is apparently NMR silent.

Although the borenium cation of **3** is planar and the vacant p orbital is fully accessible, this reactivity demonstrates that the steric demands of donors can divert the reaction pathway from classical Lewis acid–base reactivity. This is conceptually reminiscent of the reaction of $Mes_2PH$ with $B(C_6F_5)_3$ in which the reaction does not take place at the B center, but rather at a peripheral atom, affording, in that case, $Mes_2PH(C_6F_4)BF(C_6F_5)_2$.[16] However, in contrast to the present borenium cation, it can be envisioned that the B-fluoroarene substituents may have a role in generating steric protection of the vacant p orbital in $B(C_6F_5)_3$. The observation of these divergent reaction pathways also brings to mind the reaction of $R_3P/B(C_6F_5)_3$ combinations with alkynes, where the course the reaction affords either FLP addition or alkyne deprotonation products depending on the basicity of the phosphine.[17]

In conclusion, we have exploited selective dehydrogenative cationic borylation to give singly or doubly ring closed NHC–borenium salts **2** and **3**. The planar borenium cation salt in **3** reacts with donors to either give classical Lewis acid–base reactivity or to effect deprotonation of the benzylic carbons affording the unusual salt **7** containing three boron centers in the cation. It is clear that this reactivity provides a means to prepare extended π systems containing planar borenium centers and a method by which they may be functionalized at the periphery. We are continuing to examine this reactivity targeting new systems suitable for either catalysis or applications in photochemistry or materials science.

**Keywords:** boranes · borylation · carbenes · frustrated Lewis pairs · steric hindrance

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[18] CCDC-1040279 (**1**), 1040280 (**2**), 1040281 (**3**), 1040282 (**4**), and 1040283 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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