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**Title:** Divergent reactivity of nucleophilic 1-bora-7a-azaindenide anions

**Year:** 2018

**Version:** Accepted version (Final draft)

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**Please cite the original version:**

Morgan, M. M., Rautiainen, M., Piers, W. E., Tuononen, H., & Gendy, C. (2018). Divergent reactivity of nucleophilic 1-bora-7a-azaindenide anions. *Dalton Transactions*, 3(47), 734-741. <https://doi.org/10.1039/C7DT04350C>

# Divergent reactivity of nucleophilic 1-bora-7a-azaindenide anions.†‡

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

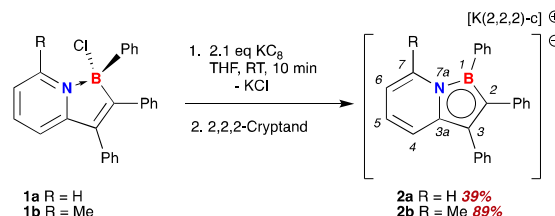
The reactions of 1-bora-7a-azaindenide anions, prepared in moderate to excellent yields by reduction of the appropriate 1-bora-7a-azaindenyl chlorides with  $\text{KC}_8$  in THF, with alkyl halides and carbon dioxide were studied. With alkyl halides ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{I}$  and  $\text{BrCH}(\text{D})\text{CH}(\text{D})^t\text{Bu}$ ), the anions behave as boron anions, alkylating the boron center via a classic  $\text{S}_{\text{N}}2$  mechanism. This was established with DFT methods and via experiments utilizing the neo-hexyl stereoprobe  $\text{BrCH}(\text{D})\text{CH}(\text{D})^t\text{Bu}$ . These reactions were in part driven by a re-aromatization of the six membered pyridyl ring upon formation of the product. Conversely, in the reaction of the 1-bora-7a-azaindenide anions with  $\text{CO}_2$ , a novel carboxylation of the C-2 carbon alpha to boron was observed. Computations indicated that while carboxylation of the boron center was kinetically feasible, the products of B-carboxylation were not thermodynamically favored relative to the observed C-2 carboxylated species, which were formed preferably due to the generation of both C-C and B-O bonds. In these products, the pyridyl ring remains non-aromatic, in part accounting for the observed reversibility of carboxylation.

## Introduction

The synthesis and evaluation of BN isosteres of archetypal aromatic hydrocarbons has been a fruitful and active area of research in main group and organic materials chemistry in the past decade.<sup>1–6</sup> The substitution of a C=C double bond with the more polarized B=N unit within a larger aromatic framework can have beneficial effects on the packing,<sup>7, 8</sup> absorption<sup>9, 10</sup> and electron transporting<sup>11, 12</sup> properties of the molecules and materials compared to the all carbon frameworks.<sup>13</sup> As such, there has also been significant interest in defining the differences between all carbon and BN compounds at a more fundamental level in the most basic building units of polycyclic aromatic hydrocarbons (PAHs). The groups of Liu<sup>14</sup> and Braunschweig,<sup>15</sup> for example, have developed general syntheses of all three possible isomers of azaborines, BN analogs of benzene, and evaluated the physical properties and reactivity of these compounds in detail.<sup>16–23</sup> The undertaking of similar studies on even simple polycyclic building blocks becomes more complex due to heightened numbers of possible BN isomers, but investigations into the exhaustive evaluation of BN analogs of naphthalene<sup>24–26</sup> and other PAHs<sup>27,</sup>

<sup>28</sup> have been initiated.

Indene and the indenide anion constitute another basic building block in PAH chemistry<sup>29–33</sup> and there has also been recent interest in BN isosteres of this unit.<sup>34–38</sup> Here, even only considering 1,2 BN compounds, there are 10 possible BN indenide isomers, (see Scheme S1 in the ESI†) and so the mapping of properties and stabilities of each isomer is a complex endeavour just from a synthetic perspective. We recently reported a zirconocene mediated synthesis of the 1-bora-7a-azaindene framework represented by compounds **1a–b** (Scheme 1)<sup>34</sup> which is one of the possible 1,2-BN analogs of indene. Our synthesis differs from others reported<sup>35,36</sup> in that the boron centre remains functionalized with a halide, and so the compound can be readily reduced by two electrons to form the 1-bora-7a-azaindenide anions **2a–b** as shown. The syntheses can be carried out in gram quantities which has made it possible to conduct reactivity studies of these anions with electrophiles. Here we report two different reaction paths for these BN indenides, highlighting how aromaticity changes can dictate reaction paths and lead to unique reactivity in comparison to that observed in analogous reactions in the all-carbon reaction manifold.



Scheme 1. Synthesis of 1-bora-7a-azaindenide anions **2**.

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† Dedicated to Prof. Phil Power, a giant of modern main group chemistry, on the occasion of his 65<sup>th</sup> birthday.

‡ Electronic Supplementary Information (ESI) available: Description of general methods, computational methods and results, Figures S1–11 and crystallographic data for **4** and **6a**. CCDC 1584567–1584568. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt04350c.

## Results and Discussion

Compounds **1a** and **2a** were reported previously,<sup>34</sup> and the methylated derivatives **1b** and **2b** were prepared analogously using 2-methyl pyridine in the zirconocene synthetic sequence. The 1-bora-7a-azaindenides **2** can be prepared without using the cryptand potassium ion sequestering agent but the K(2,2,2-c) salts are more easily handled and were therefore used throughout this study. As reported previously,<sup>34</sup> NICS calculations on these anions indicate that the five-membered C<sub>3</sub>BN ring has significant aromaticity associated with it (the NICS(1) and NICS(0) values are -11.4 and -12.5, respectively, for **2a**; a complete listing of NICS values computed for all compounds reported here can be found in Table S1). Conversely, the six-membered ring, with NICS values near 0, is essentially non-aromatic. This is reflected in the chemical shifts associated with the C-H protons of this ring in **2a** and **2b**, which are significantly upfield shifted in the <sup>1</sup>H NMR spectrum, particularly the C-H<sub>5</sub> and C-H<sub>6</sub> protons. In **2a**, they appear at 5.66 and 5.59 ppm, respectively, while in **2b**, they arise at 5.49 and 5.28 ppm. These shifts are more consistent with a diene moiety than a pyridyl group. As reported earlier,<sup>34</sup> the striking bond length alternation in the structure of **2a** is completely consistent with this picture of the molecule (see Scheme S2). Molecular orbital analysis of the occupied  $\pi$  orbitals of an unsubstituted model of **2a** (Fig. 1, top) in comparison to the all carbon indenide anion also supports the description of delocalized bonds in five-membered BN-containing ring. Four of the  $\pi$  orbitals are bonding and one is anti-bonding with respect to each of the bonds of the five-membered ring, apart from the transannular C-N bond for which only three  $\pi$  orbitals are bonding and two are anti-bonding. Similarly, the  $\pi$  orbitals support the localization of  $\pi$  electrons to two double bonds C4-C5 and C6-C7 in the six-membered ring.

Given this analysis, it is perhaps not surprising that an evaluation of the charge distribution (electrostatic potential) within the 1-bora-7a-azaindenide anion (Fig. 1, bottom) indicates that the electron rich areas of the molecule are mainly associated with the five-membered ring. Within this ring, C-2 and the boron atom have the most negative surface values, indicating the most likely sites for an attack by electrophiles, while the electrostatic potential on C-3 is less negative. This contrasts with the all carbon indenide ion itself, wherein the most electron rich areas are associated with the C-1/C-3 positions. We thus explored the reactions of anions **2a** and **2b** with simple electrophiles to ascertain the impact of this unusual charge distribution on the outcome of the reactions.

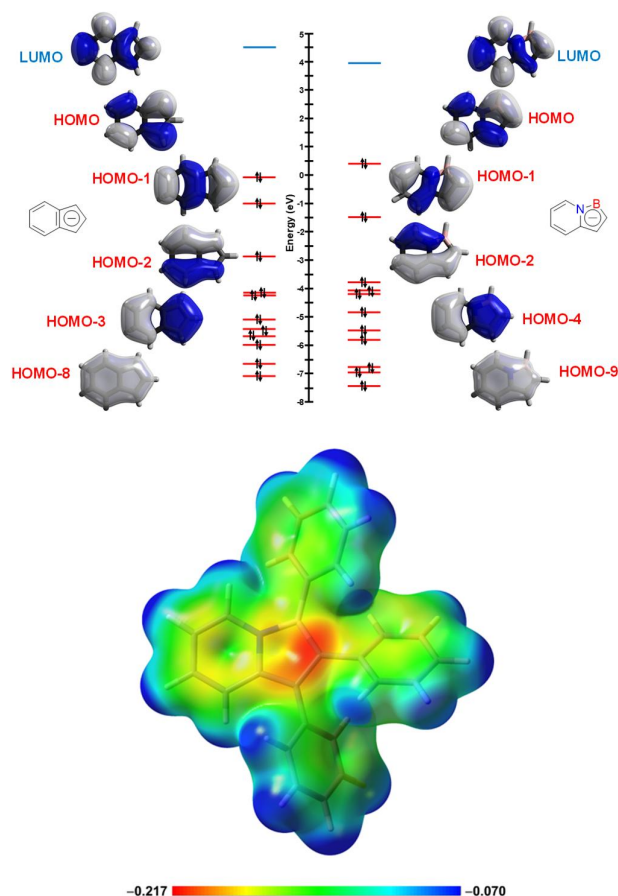
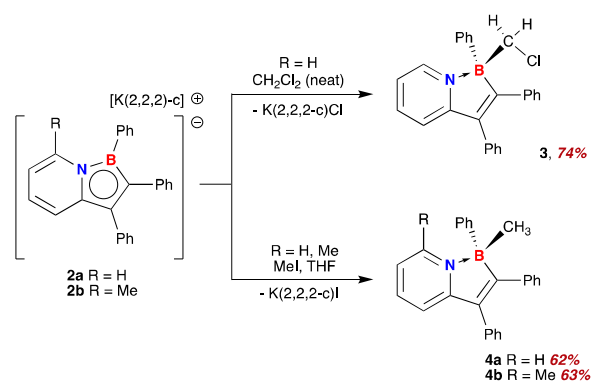


Fig. 1. Top: Highest occupied  $\pi$  orbitals of indenide (left) and 1-bora-7a-azaindenide (right). Bottom: Electrostatic potential [atomic units (au)] of **2a** mapped on the electron density isosurface (0.005 au) at PBE0/def-TZVP level of theory.

It was apparent early in our investigations that **2a** was not stable in the presence of alkyl halides; attempts to obtain the <sup>1</sup>H NMR spectrum of **2a** in CD<sub>2</sub>Cl<sub>2</sub> resulted in immediate and clean conversion to a new product as judged by a dark orange to pale yellow colour change and NMR spectroscopy. The characteristic <sup>11</sup>B NMR chemical shift of 24.5 ppm for **2a** shifted upfield to 1.9 ppm, in the range of neutral, four-coordinate borane compounds, and the C-H<sub>4-7</sub> protons of the pyridyl unit all shifted downfield significantly, indicating a re-aromatization of this ring in comparison to **2a**. Furthermore, when CH<sub>2</sub>Cl<sub>2</sub> was employed, an AB quartet at 3.62 and 3.48 ppm (<sup>2</sup>J<sub>HH</sub> = 12.5 Hz) was observed for the diastereotopic protons deriving from the DCM electrophile in the product. While the electrostatic map in Fig. 1 suggests that C-2 might be the most nucleophilic site in the ring, subsequent investigations showed the product of this reaction to be the 1-chloromethyl-1-bora-7a-azaindenyl derivative **3** (Scheme 2). This was confirmed *via* a partial structural determination (connectivity only) on single crystals, and by the synthesis of



Scheme 2. Reactions of 1-bora-7a-azaindenide anions **2** with alkyl halides.

the analogous methyl compounds, **4a-b**, prepared by reaction of **2a-b** with methyl iodide in good yields. For derivative **4a**, the molecular structure was determined (Fig. 2) and clearly establishes that the alkyl groups in these reactions add to the boron centre. The metrical parameters for **4a** support the notion that the pyridyl ring has re-aromatized, and a longer B1-N1 bond of 1.6198(16) Å compared to the distance of 1.438(4) Å in **2a** is also consistent with conversion from a 1-bora-7a-azaindenide to an indenyl derivative.

These observations indicate that **2a** functions as a rare example of anionic boron nucleophile<sup>39–43</sup> in its reactions with alkyl halides, despite the more pronounced localization of negative charge on the C-2 carbon of the 1-bora-7a-azaindenide anion. Given that the indenide anion itself alkylates exclusively at the C-1/C-3 positions,<sup>44</sup> it is notable that no evidence for alkylation of the C-3 position in anions **2** was observed. Density functional theory investigation of the reaction of **2a** with CH<sub>2</sub>Cl<sub>2</sub> shows that the lowest energy reaction path involves direct S<sub>N</sub>2 type attack of the boron on the alkyl halide (Fig. 3) while attempts to locate a transition state involving C-2 attack on the substrate were not successful.

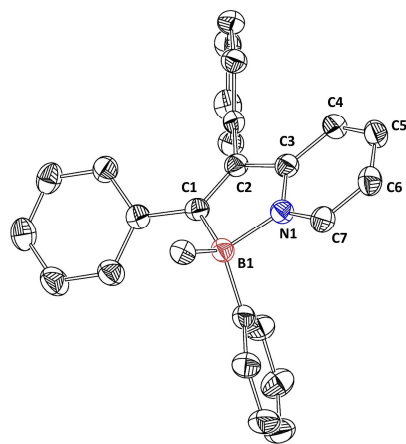


Fig. 2 Molecular structure of **4a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): B(1)–N(1), 1.6198(16); B(1)–C(1), 1.6218(18); C(1)–C(2), 1.3599(18); C(2)–C(3), 1.4596(18); C(3)–C(4), 1.3962(18); C(4)–C(5), 1.379(2); C(5)–C(6), 1.388(2); C(6)–C(7), 1.3742(19); C(7)–N(1), 1.3404(17); N(1)–C(3), 1.3571(16).

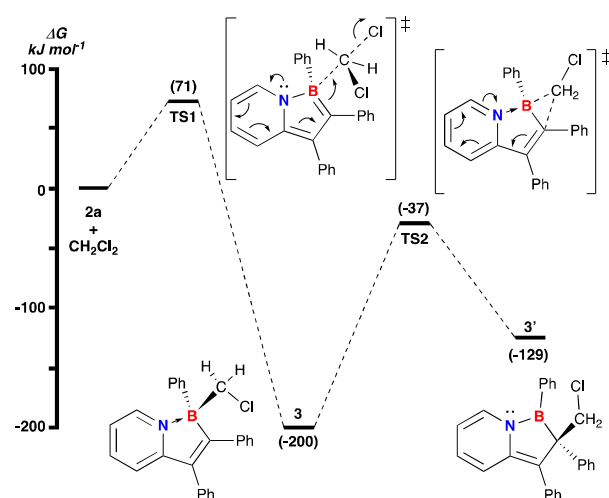
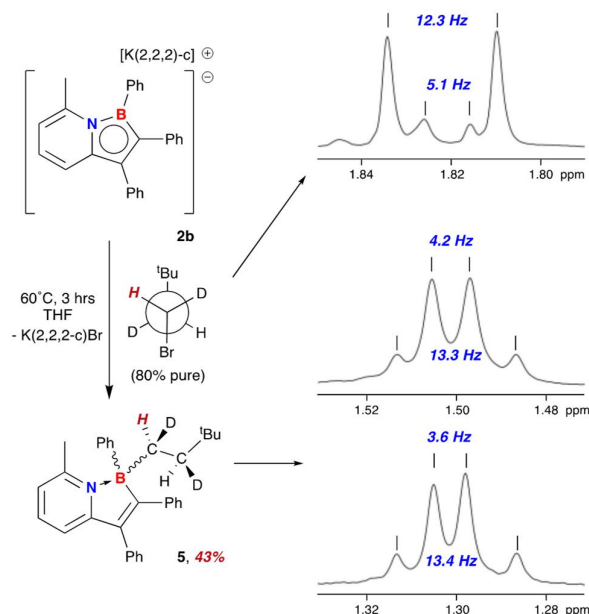


Fig. 3 Calculated Gibbs free energies (kJ mol<sup>−1</sup>, PBE0/def-TZVP level of theory) for the reaction of **2a** with CH<sub>2</sub>Cl<sub>2</sub> in dichloromethane to give either **3** or **3'**.

The boron displacement of chloride and B–C bond formation occurs through a transition state (TS1) with a barrier of 71 kJ mol<sup>−1</sup> to yield product **3** in a strongly exergonic reaction (−200 kJ mol<sup>−1</sup>). Although it was possible to locate a transition state (TS2) for transfer of a CH<sub>2</sub>Cl<sup>+</sup> fragment to C-2 starting from **3**, it had a very high activation barrier (163 kJ mol<sup>−1</sup>) and the product of the reaction, **3'**, is less stable than **3** by 71 kJ mol<sup>−1</sup>. We attribute this to the fact that, for **3**, the formation of the B–C bond is accompanied by re-aromatization of the pyridine ring (a NICS(1) value of −8.2 is calculated for this ring in **3**, see Table S1) while in **3'**, the ring remains non-aromatic (NICS(1) = 2.5) and the five membered ring also loses aromaticity (NICS(1) = 0.3) as compared to **2a**. Thus, the overall regiochemistry of this alkylation is determined to a large degree by the changes in aromaticity in **3/3'** vs. the starting materials.

To provide experimental support for the computed transition state, the 7-methyl-1-bora-7a-azaindenide **2b** was treated with the alkyl bromide 1-bromo-1,2-dideuterio-3,3-dimethylbutane. The dideuterated neo-hexyl group is a useful stereoprobe for acquiring mechanistic information because the change in stereochemistry at C-1 is easily monitored by <sup>1</sup>H NMR spectroscopy.<sup>45</sup> The bromo alkyl substrate was prepared via hydrozirconation methodology as an 80:20 mixture of *erythro*:*threo* diastereomers using a literature procedure<sup>46</sup> and reacted with **2b**.<sup>5</sup> A clean reaction to a new product (**5**, Fig. 4) was observed, but it required heating at 60 °C for 3 hours to go to completion due to the greater steric bulk of this substrate. For an S<sub>N</sub>2 mechanism, inversion of stereochemistry would be expected<sup>46</sup> in the alkylborane product, while mechanisms involving, for example, electron transfer<sup>47</sup> from **2** to the substrate, would lead to racemization. The experiment is somewhat complicated by the fact that the boron center in the alkylated product **5** is also a stereocentre. There is no diastereoselectivity observed in the formation of this stereocentre, so four signals are observed for the protons of the stereoprobe in the product's <sup>1</sup>H{<sup>2</sup>H} NMR spectrum. As can be seen in Fig. 4, the <sup>1</sup>H NMR signal associated with the proton



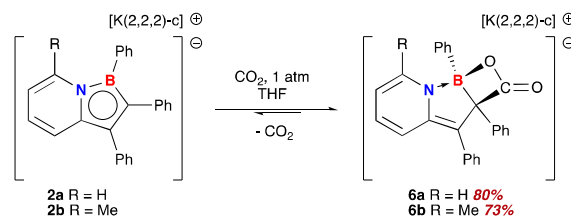
**Fig. 4** Reaction of **2b** with an 80:20 *erythro:threo* mixture of 1-bromo-1,2-dideutero-3,3-dimethylbutane. The  $^1\text{H}$  NMR spectra illustrate clean inversion to an 80:20 *threo:erythro* mixture in the 1:1 mixture of B-diastereomeric products of  $\text{S}_{\text{N}}2$  alkylation, **5**.

in the 2-position of the probe is well resolved and indicates that the probe has cleanly undergone conversion to an 80:20 mixture of *threo:erythro* isomers, as would be expected for an  $\text{S}_{\text{N}}2$  mechanism and therefore completely consistent with the computations presented above. Thus, these 1-bora-7a-azaindenides behave as pure  $\text{S}_{\text{N}}2$  nucleophiles to alkyl halides and the involvement of SET reaction mechanisms<sup>47</sup> is negligible for this class of boron anions. Another topical area of research in main group chemistry involves the “metal-free” binding and activation of small molecules,<sup>9</sup> particularly carbon dioxide<sup>48–54</sup> ( $\text{CO}_2$ ). Compounds **2** undergo an immediate reaction with the electrophile  $\text{CO}_2$ , as indicated by a dark orange to deep red colour change upon exposure of THF solutions to 1 atm of  $\text{CO}_2$ . *In situ* NMR spectroscopy indicates that the reaction proceeds cleanly to one product; by analogy to the reactions with alkyl halides, initially it was postulated that the boron nucleophile attacked the electrophilic carbon of  $\text{CO}_2$ . However, while the  $^{11}\text{B}$  NMR spectrum exhibited a signal at 5.3 ppm, consistent with four-coordinate boron, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum contained a sharp signal at 176.0 ppm for the carbon in the product derived from  $\text{CO}_2$ . This was confirmed by using  $^{13}\text{CO}_2$ . If bonded to boron, this signal would be expected to be significantly broadened due to proximity to the quadrupolar boron centre. Furthermore, in the  $^1\text{H}$  NMR spectrum, the signals for the pyridyl ring C-H groups remain upfield shifted (C-H<sub>5</sub> = 6.21 ppm; C-H<sub>6</sub> = 4.94 ppm), suggesting that re-aromatization of the pyridyl ring is *not* featured in the product of this reaction. X-ray crystallography on the product of the reaction of **2a** with  $\text{CO}_2$  revealed the structure of the products **6a-b** to be as depicted in Scheme 3 and Fig. 5, wherein the electrophilic carbon of  $\text{CO}_2$  has been attacked by C-2 of the 1-bora-7a-indenide ring. Note that, although only

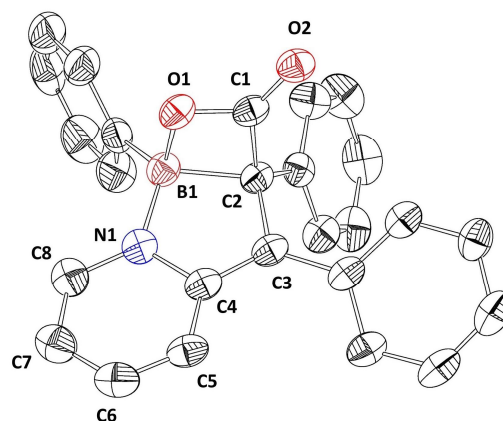
one enantiomer is shown in Scheme 3, the reaction is not enantioselective, but essentially 100% diastereoselective due to the constraints of the B(1)-O(1)-C(1)-C(2) ring.

The ions in compound **6a** are well separated in the solid state; Fig. 5 shows only the anion, and reveals that the  $\text{CO}_2$  has been added across the C(2)-B(1) bond. The C(1)-O(1) bond length of 1.334(3) Å is significantly lengthened compared to the 1.208(3) Å distance for C(1)-O(2); a stretching vibration of 1709  $\text{cm}^{-1}$  in the IR spectrum of **6a** is also consistent with a C(1)-O(2) double bond. Short bond lengths for C(3)-C(4), C(5)-C(6) and C(7)-C(8) alternate with longer lengths C(4)-C(5) and C(6)-C(7), indicating bond localization within the bicyclic framework and non-aromaticity within both rings. NICS(1) values of 0.2 for the pyridyl and -1.0 for the five-membered ring (see Table S1) support this notion; upon addition of  $\text{CO}_2$  to compounds **2**, the aromaticity of the five-membered ring is disrupted, while the pyridyl ring remains non-aromatic.

The binding of  $\text{CO}_2$  to these compounds was found to be reversible in solution. When solutions of **6a** were exposed to  $^{13}\text{CO}_2$ , incorporation of the labelled carbon dioxide into **6a** was facile. Furthermore, when **6a** was treated with excess  $\text{CH}_2\text{Cl}_2$ , slow, irreversible conversion of the compound to compound **3** was observed. Presumably, the  $\text{CO}_2$  is released from **6a** and **2a**

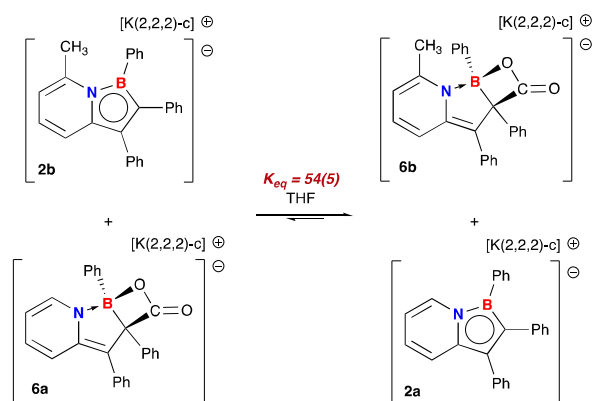


**Scheme 3.** Reactions of 1-bora-7a-azaindene anions **2a-b** with carbon dioxide.



**Fig. 5** Molecular structure of the anion of **6a**. Hydrogen atoms and the (2,2,2-c) potassium ion have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): B(1)-O(1), 1.562(3); B(1)-N(1), 1.534(4); B(1)-C(2), 1.665(4); C(2)-C(3), 1.525(3); C(3)-C(4), 1.371(4); C(4)-C(5), 1.447(4); C(5)-C(6), 1.354(4); C(6)-C(7), 1.420(5); C(7)-C(8), 1.363(4); C(8)-N(1), 1.355(4); N(1)-C(4), 1.405(3); C(1)-C(2), 1.530(3); C(1)-O(1), 1.334(3); C(1)-O(2), 1.208(3). Selected bond angles (°): O(1)-B(1)-C(2), 86.01(18); C(1)-C(2)-B(1), 80.75(18); O(1)-C(1)-C(2), 100.3(2); B(1)-O(2)-C(1), 91.04(18); O(1)-C(1)-O(2), 125.9(2).



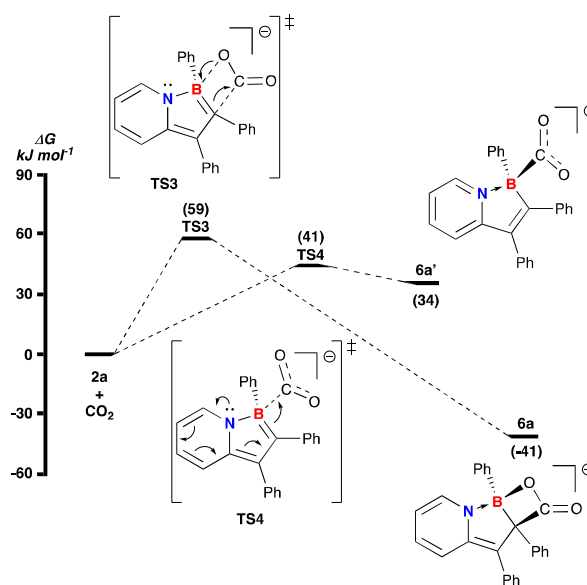


**Scheme 4.** Equilibrium constant measurement at room temperature for  $\text{CO}_2$  binding to compounds **2a** and **2b**.

is trapped by the DCM *via* the  $\text{S}_{\text{N}}2$  reaction discussed above. This reversibility enabled us to probe the relative affinity of **2a** and **2b** for binding  $\text{CO}_2$  (Scheme 4). When freshly isolated **6a** or **6b** was dissolved in THF with one equivalent of **2b** or **2a**, respectively, the equilibrium established over the course of a few hours indicated that the  $\text{CO}_2$  adduct **6b** is strongly favoured over **6a**;  $K_{\text{eq}}$  at 298 K was measured by  $^1\text{H}$  NMR spectroscopy to be 54(5).<sup>||</sup> This is in keeping with the notion that methyl substituted **2b** is a more electron rich anion that acts as a stronger nucleophile to RX or  $\text{CO}_2$  electrophiles.

The addition of  $\text{CO}_2$  to C-2 in compounds **2a-b** directly contrasts with what is observed when the all-carbon indenide anion is trapped with  $\text{CO}_2$ . Here,  $\text{CO}_2$  adds exclusively to the C-1 position resulting in indene-1-carboxylic acid or indene-3-carboxylic acid, depending on the nature of the work up procedure.<sup>55, 56</sup> The reaction of **2a** with  $\text{CO}_2$  was probed computationally (Fig. 6) and while a transition state (TS4) was located for attack of the  $\text{CO}_2$  by the nucleophilic boron centre, the product of this reaction (**6a'** in Fig. 6) is 34  $\text{kJ mol}^{-1}$  less stable than the starting materials. Hence, the reverse reaction is essentially barrierless and the equilibrium favours **2a** and  $\text{CO}_2$ . The transition state TS3 for attack of  $\text{CO}_2$  by C-2 (TS3), while slightly higher than TS4, is nonetheless readily accessible with an energy of only 59  $\text{kJ mol}^{-1}$  above the starting materials.

This transition state leads directly to product **6a** in a moderately exergonic reaction (41  $\text{kJ mol}^{-1}$ ) which, despite the non-aromatic character of both rings and the absence of re-aromatization as a driving force is favoured by the formation of both new C-C and B-O bonds. Still, the barrier to  $\text{CO}_2$  loss is only 100  $\text{kJ mol}^{-1}$  which is consistent with the observed tendency of **6a** to lose  $\text{CO}_2$  at room temperature.



**Fig. 6** Calculated Gibbs free energies ( $\text{kJ mol}^{-1}$ , PBE0/def-TZVP level of theory) for the reaction of **2a** with  $\text{CO}_2$  in toluene to give either **6a** or **6a'**.

## Conclusions

The study described here was aimed at examining the effects of BN substitution within the indenide framework on the course of reactions with simple electrophiles. We specifically utilized 1-bora-7a-azaindenide anions, prepared using organozirconocene based methods, one of ten possible BN indenide isomers. We found that the locus of electrophilic attack was confined to the five-membered BN containing ring, but that the regiochemistry observed was dependent on the nature of the electrophile. Alkyl halides reacted at the boron atom to give neutral BN-indenyl products in which the six-membered pyridyl ring is re-aromatized, a strong factor in determining the outcome of the reaction. This reactivity bears some similarity to what is observed in the reactions of the all carbon indenide anion with alkyl halides, which alkylate at the C-1/3 positions. The reactions of **2a-b** with  $\text{CO}_2$ , however, differs from the analogous reactivity in the indenides in that the  $\text{CO}_2$  electrophile adds to the C-2 carbon of the 1-bora-7a-azaindenides. Here, the Lewis base/Lewis acid nature of these BN compounds conspires to bind the  $\text{CO}_2$  without re-aromatizing the pyridyl ring. For this reason, the bonding of  $\text{CO}_2$  to compounds **2** is reversible at room temperature.

## Experimental

For general experimental details and a description of the synthesis of compound **1b** and **2b**, see the ESI†.

### Synthesis of 3

In a glovebox, a 50ml two-neck round bottom flask was charged with **1a** (100 mg, 0.263 mmol) in 15 mL of THF.  $\text{KC}_8$  (75 mg, 0.552 mmol) was added and the flask attached to a

swivel frit apparatus. The reaction was allowed to stir under argon for 10 minutes.  $\text{CH}_2\text{Cl}_2$  was vacuum transferred into the flask, turning the dark orange solution into a clear colorless solution. Graphite was filtered off through the frit and solvent removed giving a pale yellow solid. This was then passed through a silica plug using dichloromethane to yield **3** as a white solid (76 mg, 0.20 mmol, 74%).  $^1\text{H}$  NMR (500 MHz, methylene chloride- $d_2$ )  $\delta$  8.36 (dd,  $J$  = 5.7, 1.3 Hz, 1H, PyH), 7.99 (ddd,  $J$  = 8.7, 7.5, 1.5 Hz, 1H, PyH), 7.48 (d,  $J$  = 8.2 Hz, 1H, PyH), 7.43 – 7.30 (m, 6H, ArH), 7.25 – 7.16 (m, 5H, ArH/PyH), 7.11 – 7.08 (m, 3H, ArH), 6.98 – 6.95 (m, 2H, ArH), 3.62 (d,  $J$  = 12.5 Hz, 1H,  $\text{CH}_2\text{Cl}$ ), 3.48 (d,  $J$  = 12.5 Hz, 1H,  $\text{CH}_2\text{Cl}$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  161.03, 141.90, 140.42, 139.07, 135.29, 134.77, 131.48, 129.43, 128.11, 127.78, 127.09, 126.97, 126.83, 125.91, 125.60, 119.58, 118.45, 40.90 (br).  $^{11}\text{B}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.89. Elemental analysis calculated C 79.32; H 5.38; N 3.56, Found, C 79.44, H 5.26, N 3.55.

#### Synthesis of 4a

In a glovebox, a 50 ml two-neck round bottom flask was charged with **1a** (106 mg, 0.279 mmol) in 15 mL of THF.  $\text{K}_2\text{C}_8$  (75 mg, 0.558 mmol) was added and the flask attached to a swivel frit apparatus. The reaction was allowed to stir under argon for 10 minutes. MeI (0.1 mL, 1.61 mmol) was added dropwise to the reaction, turning the dark orange solution into a clear colorless solution. Solvent was removed under vacuum and 10 mL of dichloromethane was added. Graphite and KCl were filtered off through the frit and solvent removed to yield **4a** as a white solid (62 mg, 0.17 mmol, 62%).  $^1\text{H}$  NMR (500 MHz, methylene chloride- $d_2$ )  $\delta$  8.20 (d,  $J$  = 5.6 Hz, 1H, PyH), 7.92 – 7.85 (m, 1H, PyH), 7.45 – 7.39 (m, 3H ArH/PyH), 7.39 – 7.32 (m, 3H ArH), 7.29 – 7.25 (m, 2H), 7.24 – 7.16 (m, 4H, ArH/PyH), 7.15 – 7.10 (m, 1H ArH), 7.08 – 7.03 (m, 2H, ArH), 7.01 – 6.98 (m, 2H, ArH), 0.43 (s, 3H, BMeH).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  179.78(br), 160.04, 149.54(br), 141.57, 139.30, 135.52, 132.95, 132.46, 131.41, 129.52, 128.15, 128.09, 126.83, 126.81, 126.62, 125.75, 124.98, 119.15, 118.21, 5.48(br).  $^{11}\text{B}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.96. Elemental analysis calculated C 86.92; H 6.17; N 3.90, Found C 86.57, H 6.15, N 3.76.

#### Synthesis of 4b

In the glovebox, a 50 ml two-neck round bottom flask was charged with **1b** (92 mg, 0.234 mmol) in 15 mL of THF.  $\text{K}_2\text{C}_8$  (66 mg, 0.491 mmol) was added and the flask attached to a swivel frit apparatus. The reaction was allowed to stir under argon for 10 minutes. MeI (0.1 mL, 1.61 mmol) was added dropwise to the reaction, turning the dark orange solution into a clear colorless solution. Solvent was removed under vacuum and 10 mL of dichloromethane was added. Graphite and KCl were filtered off through the frit and solvent removed to yield **4b** as a white solid (55 mg, 0.15 mmol, 63%).  $^1\text{H}$  NMR (500 MHz, THF- $d_8$ )  $\delta$  7.85 (t,  $J$  = 7.8 Hz, 1H, PyH), 7.36 – 7.30 (m, 3H), 7.30 – 7.24 (m, 4H, Ar/PyH), 7.21 (d,  $J$  = 6.7 Hz, 2H, ArH), 7.15 (td,  $J$  = 8.1, 7.7, 6.2 Hz, 2H, ArH), 7.11 – 7.06 (m, 2H, ArH), 6.94 – 6.90 (m, 2H, Ar/PyH), 6.75 (m, 2H, ArH), 2.38 (s, 3H, PyMeH), 0.38

(s, 3H, BMeH).  $^{13}\text{C}$  NMR (126 MHz, THF- $d_8$ )  $\delta$  161.26, 154.71, 139.18, 135.73, 132.69, 132.53, 131.49, 129.64, 127.91, 127.58, 126.77, 126.59, 126.40, 125.28, 124.65, 120.66, 115.56, 20.14, 1.63 MeC. *Note: Two of the carbons attached to boron are not observed.*  $^{11}\text{B}$  NMR (161 MHz, THF- $d_8$ )  $\delta$  2.86. Elemental analysis calculated C 86.87; H 6.48; N 3.75, Found C 86.81, H 6.40, N 3.69.

#### Synthesis of 5

In a two-neck 50 mL round bottom flask **1b** (50 mg, 0.13 mmol) was taken up in THF (15 mL). To this was added solid  $\text{K}_2\text{C}_8$  (37 mg, 0.27 mmol), turning the pale yellow solution a dark orange with a black precipitate of graphite forming immediately. The flask was then attached to a swivel frit apparatus and the reaction allowed to stir under argon for 10 minutes. A solution of the dideuterated neohexyl stereoprobe (24 mg, 0.14 mmol) in THF (2 mL) was added via syringe turning the dark orange solution a more pale yellow. This was heated at 60 °C for three hours before the solvent was removed in vacuo and taken back up into  $\text{CH}_2\text{Cl}_2$  (25 mL) and filtered through the swivel frit to remove the graphite. The collected solution was passed through a silica plug with  $\text{CH}_2\text{Cl}_2$  in the atmosphere, which after removal of solvent yielded **5** as a white solid (25 mg, 0.056 mmol, 43%).  $^1\text{H}$  NMR (500 MHz, Benzene- $d_6$ )  $\delta$  7.50 (d,  $J$  = 7.2 Hz, 2H, ArH), 7.33 (dd,  $J$  = 8.3, 7.1 Hz, 2H, ArH), 7.27 – 7.20 (m, 3H), 7.16 – 6.99 (m, 5H), 6.96 – 6.86 (m, 3H), 6.86 – 6.74 (m, 2H), 6.08 – 6.03 (m, 1H), 2.07 (d,  $J$  = 1.6 Hz, 3H), 1.50 (m, 0.5H, BChD), 1.30 (m, 0.5H, BChD), 1.16 (m, 0.5H, CHDCHD $t$ Bu), 0.89 (s, 9H,  $t$ BuH), 0.63 (m, 0.5H, CHDCHD $t$ Bu).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  161.84, 154.26, 147.39(br), 139.88, 138.47, 135.73, 133.54, 131.75, 129.78, 128.00, 127.81, 126.30, 125.72, 125.22, 119.73, 115.03, 38.61(br), 30.05, 28.71, 19.63, 11.28(br). *Note: Two of the carbons attached to boron are not observed.*  $^{11}\text{B}$  NMR (161 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.05. Elemental analysis calculated C 86.28, H 8.15, N 3.14, Found C 85.98, H 8.03, N 3.28.

#### Synthesis of 6a

In a J young NMR tube, **2a** (10 mg) was taken up in THF- $d_8$  (0.7 mL). The solution was degassed and placed under one atmosphere of  $\text{CO}_2$ . After shaking the NMR tube for 5 minutes the sparingly soluble **2a** was completely dissolved and the dark orange solution had turned a dark red colour, NMR of this showed quantitative conversion to **6a**. When the THF solution was layered with pentane in the glove box, X-ray quality crystals of **6a** were obtained (8 mg, 80% yield).  $^1\text{H}$  NMR (500 MHz, THF- $d_8$ )  $\delta$  7.56 – 7.47 (m, 2H, ArH), 7.29 – 7.22 (m, 2H, ArH), 6.96 – 6.92 (m, 4H), 6.88 (td,  $J$  = 8.6, 7.2 Hz, 3H, Ar/PyH), 6.78 – 6.69 (m, 3H, Ar/PyH), 6.61 – 6.47 (m, 3H), 6.22 (ddd,  $J$  = 9.6, 5.9, 1.6 Hz, 1H, PyH), 4.94 (td,  $J$  = 6.2, 1.2 Hz, 1H, PyH), 3.55 (s, 12H, CryptH), 3.53 – 3.46 (m, 12H, CryptH), 2.55 – 2.49 (m, 12H, CryptH).  $^{13}\text{C}$  NMR (126 MHz, THF- $d_8$ )  $\delta$  176.48( $\text{CO}_2$  C), 147.25, 143.70, 140.97, 139.54, 132.21, 129.83, 126.02, 125.94, 125.48, 125.18, 125.16, 123.81, 120.41, 118.66, 114.61, 100.07, 97.16, 69.72, 66.94, 53.30. *Note: two carbons attached to boron are not observed.*  $^{11}\text{B}$  NMR (161 MHz, THF-

$d_8$ )  $\delta$  5.30. IR (KBr pellet) 1708.97  $\text{cm}^{-1}$ . Elemental analysis calculated C 65.74, H 6.90, N 5.23, Found C 65.48, H 6.99, N 5.50.

### Synthesis of 6b

In a J young NMR tube, **2b** (10 mg) was taken up in THF- $d_8$  (0.7 mL). The solution was degassed and placed under one atmosphere of  $\text{CO}_2$ . After shaking the NMR tube for <1 minute the sparingly soluble **2b** was completely dissolved and the bright orange solution had turned a dark red colour, NMR of this showed quantitative conversion to **6b**. When the THF solution was layered with pentane in the glove box, small needlelike crystals formed (5 mg, 50%).  $^1\text{H}$  NMR (500 MHz, THF- $d_8$ )  $\delta$  7.49 – 7.42 (m, 3H, ArH), 6.84 (m, 5H, ArH, PyH), 6.72 (m, 3H, ArH), 6.61 (m, 3H, ArH), 6.52 – 6.45 (m, 1H, ArH), 6.43 – 6.37 (m, 1H, ArH), 6.13 (dd,  $J$  = 9.5, 6.0 Hz, 1H, PyH), 4.77 (d,  $J$  = 5.9 Hz, 1H, PyH), 3.54 (s, 12H, CryptH), 3.52 – 3.47 (m, 12H, CryptH), 2.54 – 2.49 (m, 12H, CryptH), 1.42 (s, 3H, MeH).  $^{13}\text{C}$  NMR (126 MHz, THF- $d_8$ )  $\delta$  173.01, 149.43, 143.90, 141.18, 130.05, 125.91, 125.82, 125.51, 125.25, 125.08, 124.35, 123.03, 120.22, 118.37, 112.33, 109.40, 98.70, 83.22, 69.73, 67.02, 53.56, 21.49. Note: two carbons attached to boron are not observed  $^{11}\text{B}$  NMR (161 MHz, THF- $d_8$ )  $\delta$  5.41. IR (KBr Pellet) 1709.63  $\text{cm}^{-1}$ . Elemental analysis calculated C 66.09, H 7.03, N 5.14, Found C 65.96, H 6.92, N 5.28.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

Funding for this work was provided by NSERC of Canada (Discovery Grant) the Canada Research Chair secretariat (Tier I CRC 2013–2020) to W. E. P. and the Academy of Finland (project #136929) and Emil Aaltonen Foundation to H. M. T. Finnish Grid and Cloud Infrastructure (urn:nbn:fi:research-infras-2016072533) is acknowledged for granting computational resources. W. E. P. acknowledges the Alexander von Humboldt Foundation for a Research Fellowship. M. M. M. thanks NSERC of Canada for PGSD Scholarship support.

### Notes and references

§ Compound **2b** was employed because it was more reactive than **2a** towards the stereoprobe and yielded **5** cleanly.

¶ Compounds **2** do not react with excess  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2$  or silanes ( $\text{Et}_3\text{SiH}$ ,  $\text{PhMe}_2\text{SiH}$ ,  $\text{PhSiH}_3$ ) at room temperature to 60  $^\circ\text{C}$ .

|| Attempts to obtain  $K_{\text{eq}}$  at different temperatures were complicated by escape of  $\text{CO}_2$  into the headspace of the NMR tube, so these measurements and a van't Hoff analysis were precluded.

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