

Synthesis and Comparative Characterization of 9-Boraanthracene, 5-Boranaphthacene, and 6-Borapentacene Stabilized by the H₂IMes Carbene**

Thomas K. Wood, Warren E. Piers,* Brian A. Keay, and Masood Parvez^[a]

Abstract: A general procedure for the preparation of three N-heterocyclic carbene stabilized, boron-containing acenes (9-boraanthracene, 5-boranaphthacene, and 6-borapentacene) is presented. The key steps involve a transmetallation reaction between BCl₃ and an appropriate stannacyclic precursor, and the dehydrochlorination of the H₂IMes adduct of the chloroborane product. Comparative structural, photophysical, and redox properties reveal narrow HOMO–LUMO gaps relative to the all-carbon acene analogues.

Keywords: aromaticity • boron • carbenes • heteroacenes • synthetic methods

Introduction

The chemistry of the higher acenes (for example, naphthalene, pentacene, and their substituted derivatives) have been the focus of intense study over the past decade.^[1] In addition to fundamental questions of extended aromaticity, interest in these molecules stems from their application in the field of organic electronics, which require organic semiconductors. Due to its high hole mobility, pentacene is currently a standard by which other p-type organic semiconductors are measured.^[2] Devices that incorporate organic semiconductors include light-emitting diodes^[1c] (OLEDs) and thin-film transistors^[3] (OTFTs) and their progression to general application promises to revolutionize the electronics industry.^[1b]

In addition to extensive substitution of the acene framework^[4] and extension to even higher acenes, such as hexacene^[5] and up, substitution of carbon atoms by heteroatoms has been explored as a means of stabilizing and/or tuning the electronic properties of the acene framework.^[6] In some instances, these efforts were directed at providing a low-energy LUMO that would impart n-type semiconductivity^[7]

and allow for “all-acene” p–n junctions. In this context, we became interested in exploring the incorporation of boron atoms^[8] into the acene framework and recently we reported the synthesis and characterization of the first neutral 9-boraanthracene, stabilized by an Arduengo carbene.^[9] The synthesis of this boraacene scaffold employed a tin–boron transmetallation strategy^[10] for preparing the requisite borocyclic precursor and was adaptable for the preparation of higher boraacenes.^[7a] Herein, we report on its implementation for the synthesis of 5-boranaphthacene and 6-borapentacene derivatives stabilized by N-heterocyclic carbene (NHC) ligands.

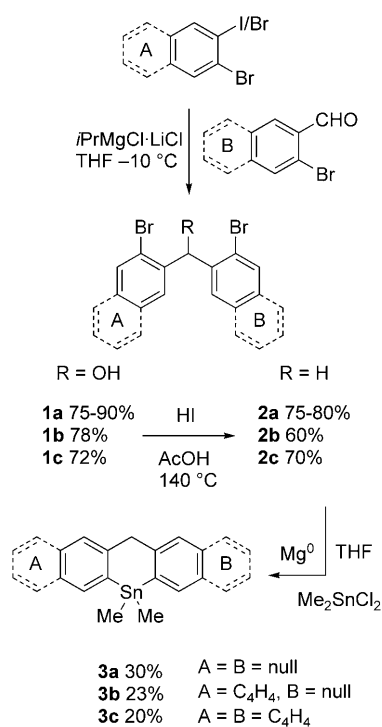
Results and Discussion

Following the steps used to prepare tricyclic stannacycle **3a**,^[9] suitable aryl halides and aldehydes were employed in the synthesis of stannacycles **3b** and **3c** as shown in Scheme 1. Treatment of 2-bromiodobenzene with *i*PrMgCl·LiCl at reduced temperature in THF generated the corresponding mono-Grignard reagent, which was quenched with 2-bromobenzaldehyde to generate symmetrically substituted methanol **1a** in good yield.^[11] Similarly 2,3-dibromonaphthalene^[12] was subjected to the same Grignard reagent exchange conditions and quenched with either 2-bromobenzaldehyde or 3-bromo-2-naphthaldehyde to give diaryl methanol derivatives **1b** and **1c**, respectively.^[12] Alcohols **1a–c** were readily reduced with hydroiodic acid in glacial acetic acid at reflux to give the corresponding diarylmetanes **2a–c**. Formation of the di-Grignard reagents from **2a–c** followed by addition of Me₂SnCl₂ gave stannacycles

[a] T. K. Wood, Prof. W. E. Piers, Prof. B. A. Keay, Prof. M. Parvez
Department of Chemistry, University of Calgary
2500 University Drive N.W. Calgary
Alberta, T1N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: wpiers@ucalgary.ca

[**] H₂IMes = 1,3-bis(2,4,6-trimethyl)imidazolidin-2-ylidene

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Scheme 1. Synthesis of stannacycles **3a–c**.

3a–c, which could be isolated by flash column chromatography.^[10a]

The primary byproducts generated during the formation of stannacycles **3a–c** were oligomeric in nature and the best results were obtained by addition of Me₂SnCl₂ to dilute solutions of the Grignard reagent by using a syringe pump. Performing the reaction at low temperature (−78 °C), extreme dilution conditions (0.01 M), or simultaneous syringe-pump addition of both reagents, had little effect on the product distribution or isolated yields of stannacycles **3**, so the 20–30% yields were accepted in order to move forward.

The ¹¹⁹Sn{¹H} NMR spectra showed singlet resonances at δ = −112, −108, and −99 ppm for **3a**, **3b**, and **3c**, respectively; these are characteristic of four coordinate organotin compounds.^[13] The presence of tin was further evidenced in the ¹H and ¹³C{¹H} NMR spectra, in that coupling to both ¹¹⁷Sn and ¹¹⁹Sn nuclei was observed for several resonances. In particular, the ¹³C{¹H} NMR spectra showed strong coupling of the tin methyl carbon atoms (average ¹J(¹¹⁹Sn,C) = 370 Hz) to the tin nuclei. Longer-range tin–carbon couplings of up to four bonds were observed for other carbon atoms in the skeleton, and most strikingly, the three-bond coupling between tin and the methylene carbon atoms were 55, 49, and 45 Hz for **3a–c**, respectively. This magnitude of ³J(Sn,C) is typical for Sn–C–C–C dihedral angles of >150°;^[14] this dihedral angle is expected to be near zero in compounds **3**, so the large coupling constant may be reflective of transannular interaction between the tin center and the methylene carbon. To probe this further, X-ray analysis of **3c** was conducted.

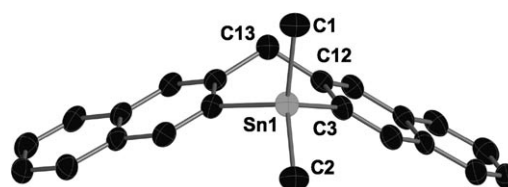
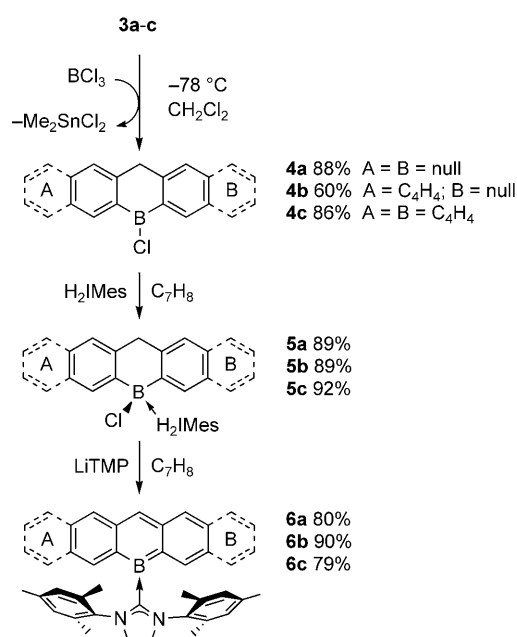


Figure 1. Thermal ellipsoid diagram (50%) of **3c**. Selected bond lengths for Sn1 [Å]: Sn1–C1, 2.138(4); Sn1–C2, 2.131(5); Sn1–C3, 2.139(2); C12–C13, 1.521(3); C12–C3 1.436(4). Selected bond and torsions angles [°]: C3–Sn1–C3', 94.03(9); C1–Sn1–C2, 117.3(2); Sn1–C3–C12, 116.4(2); C3–C12–C13, 120.0(2); Sn1–C3–C12–C13, 7.4(3).

A thermal ellipsoid diagram of **3c** is shown in Figure 1 along with selected metrical parameters. The unit cell contains three discrete molecules in which the central ring is distorted into a pseudo-boat conformation. This type of geometry alleviates ring strain that would otherwise result from the large disparity in Sn–C_{Ar} bond lengths (mean 2.143(3) Å) compared with the methylene C–C_{Ar} (mean 1.525(5) Å) bond lengths. The three molecules differ primarily in the extent of puckering in the central ring, as estimated by the angle distended between the midpoint of the vector connecting the tin and the methylene carbon and the centroids of the flanking all-carbon rings, which are 122.7° for the Sn1 molecule, 115.9° for Sn2, and 130.1° for Sn3. This puckering of the central ring places the tin atom between 3.224(3) Å (longest distance, Sn3) and 3.150(3) Å (shortest distance, Sn2) away from the methylene carbon; the sum of the van der Waals radii of these two elements is 3.87 Å.^[15] Despite the puckering observed in the solid state, no evidence in the variable temperature ¹H NMR spectra for diastereotopic methyl groups or methylene protons was observed, suggesting that ring flipping is a facile process in solution.

When **3a–c** were treated with BCl₃ (g) in CH₂Cl₂ at −78 °C and slowly warmed to room temperature, chloroboranes **4a–c** were cleanly generated in good yield. The ¹¹B NMR chemical shifts for **4a–c** were δ = 55, 56, and 54 ppm (CDCl₃), which is consistent with three-coordinate (aryl)₂BCl species.^[16] The ¹H NMR spectra of chloroboranes **4a–c** were similar in appearance to those of the stannacyclic precursors, but all resonances were shifted downfield to varying degrees, and satellites due to ¹¹⁹Sn coupling were absent. While chloroboranes **4a** and **4b** were generally well behaved in terms of solubility, borane **4c** often precipitated from reaction solutions as the boron–tin exchange proceeded and exhibited much poorer solubility in nondonor solvents. This is attributed to the sp² hybridization of the boron center, which effectively planarizes the pentacyclic framework, allowing for efficient intermolecular packing, presumably in a fashion similar to that of pentacene itself.^[1e,2a]

All of the chloroboranes **4** were highly moisture sensitive and even brief exposure to ambient conditions quickly resulted in the formation of Ar₂B–O–BAR₂ species. Thus, chloroboranes **4** were best used without purification beyond removal of the majority of the Me₂SnCl₂ byproduct by sublimation under dynamic vacuum. Obtained in this way, compounds **4a–c** were dissolved in toluene and 1,3-bis(2,4,6-tri-

Scheme 2. Synthesis of boraacenes **6a-c**.

methyl)imidazolidin-2-ylidene (H₂IMes) was added, causing the carbene–borane adducts **5a–c** to precipitate from solution, allowing for their ready isolation by filtration in excellent yield (Scheme 2). Upon ligation of the carbene to boron, the now diastereotopic benzylic protons appear as AB quartets (²*J*(H,H) = 15.4–16.4 Hz). Additionally, the ¹¹B NMR spectra of compounds **5** showed a marked change in chemical shift of approximately 60 ppm to δ = −6, −7, and −6 ppm for **5a–c**, respectively, in the range associated with neutral four-coordinate boranes. In compounds **5a** and **5c**, the ¹H NMR resonances associated with the H₂IMes fragment were all singlets, consistent with averaged C_s symmetry for these molecules.

In the instance of **5b**, however, there were multiple signals for the carbene resonances, reflecting the diastereotopic nature of these protons as a result of the lowered symmetry of the tetracyclic **5b**.

The molecular structure of **5a** was determined crystallographically and is shown in Figure 2, along with selected metrical data. Compound **5a** has a plane of symmetry that bisects atoms C9–B1–C1–Cl1. Here again the central boron-containing six-membered ring displays pseudo-boat-like geometry, similar to that observed in stannacycle **3c**. The large H₂IMes substituent occupies the sterically open axial position on the tetrahedral boron center and is oriented essentially perpendicular to the tricyclic boracycle. This allows for free rotation about the B1–C1 vector; a DFT study at the B3LYP/6-31+G(d) level^[17] in which full optimizations were performed as the H₂IMes carbene was rotated in 10° increments showed that the highest barrier to rotation of the carbene ligand is only about 5 kcal mol^{−1}.

When carbene adducts **5a–c** were suspended in toluene and treated with the lithium salt of tetramethylpiperidine (LiTMP) at room temperature, the reaction mixtures slowly changed from colorless to orange in the case of 9-boraan-

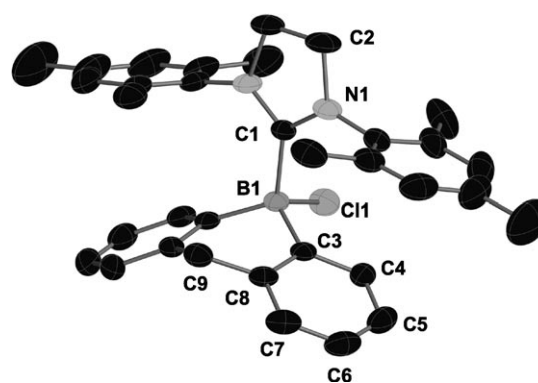


Figure 2. Thermal ellipsoid diagram (50%) of **5a**. Selected bond lengths [Å]: B1–Cl1, 1.924(3); B1–C1, 1.666(3); B1–C3, 1.613(2); C3–C4, 1.402(3); C4–C5, 1.386(3); C5–C6, 1.376(3); C6–C7, 1.384(3); C7–C8, 1.395(3); C8–C9, 1.507(2); C8–C3, 1.409(3). Selected bond and torsion angles [°]: C3–B1–C3', 108.2(2); N1–C1–B1–Cl1, −88.8(2).

thracene and darker hues for the two higher boraacenes. Spectroscopically, the generation of **6a–c** were signaled by a downfield shift in ¹¹B NMR spectra to δ = 27, 28, and 29 ppm for compounds **6a–c**, respectively, a typical region for borabenzene compounds.^[18] The ¹H NMR spectra no longer showed any resonances for the methylene protons associated with compounds **5**; instead new singlets integrating for one proton were located in the aromatic region of each spectrum. For symmetrical boraacenes **6a** and **6c**, the resonances for the H₂IMes protons appeared as four singlets in appropriate ratios, whereas for **6b** the diastereotopic nature of the carbene ligand protons was reflected in a more complex pattern of resonances. Undoubtedly, in both compounds **5** and **6**, the pattern of resonances found for the NHC ligand is related to both the compound's symmetry properties and the relative rates of B–C versus N–Mes bond rotations.^[19] Compounds **6b** and **6c**, like the previously reported **6a**,^[9] are water and air sensitive and so are best handled by using appropriate techniques.

The molecular structures of both 9-boraanthracene **6a** and 6-borapentacene **6c** were obtained; the former has been discussed in detail elsewhere.^[9] Crystals of **6c** were obtained from dichloromethane; two independent molecules exist in the unit cell and differ primarily in the level of planarity found in the borapentacene ring. For example, the average deviation from the least-squares plane defined by all atoms of the borapentacene framework for molecule 1 is 0.112 Å, whereas that for the more planar molecule 2 is only 0.069 Å. The two molecules pack in interlocked ribbons (Figure 3), in which the edges of the mesityl groups on the NHC ligand approach the faces of adjacent molecules. The closest intermolecular contacts are between the *para*-mesityl carbon atoms and the annulated carbon atoms of the central C₅B ring as indicated in Figure 3 and range between 3.76 and 3.90 Å. This packing interaction influences the curvature of the borapentacyclic portion in the two molecules. The borapentacene framework is thus aligned in a slightly offset zigzag pattern, with the closest contacts between the ends of the polycycle at about 3.6 Å, as shown.

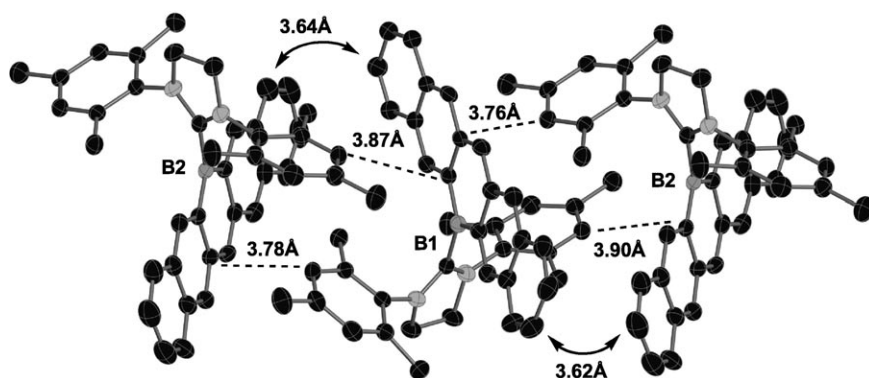


Figure 3. Packing motif of the two independent molecules of **6c**.

The metrical parameters of each molecule do not differ significantly; the molecular structure of molecule 1 is shown in Figure 4, along with selected metrical parameters. The

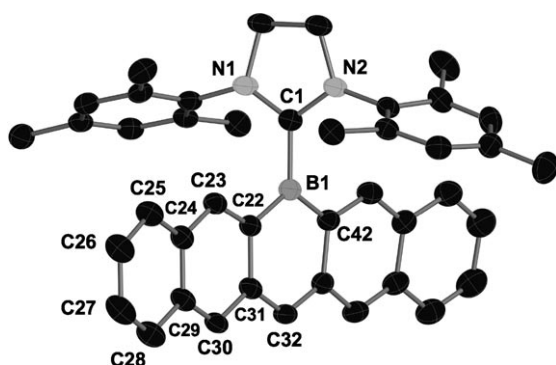


Figure 4. Thermal ellipsoid rendering (50%) of **6c**. Selected bond lengths [Å]: B1–C1, 1.612(4); B1–C22, 1.512(5); B1–C42, 1.515(5); C22–C23, 1.409(4); C23–C24, 1.392(4); C24–C25, 1.432(5); C25–C26, 1.358(5); C26–C27, 1.425(5); C27–C28, 1.353(5); C28–C29, 1.434(4); C29–C30, 1.387(5); C30–C31, 1.414(4); C31–C32, 1.406(4). Selected bond and torsion angles [°]: C1–B1–C22, 120.4(3); C1–B1–C42, 121.3(3); C22–B1–C42, 118.3(3); N1–C1–B1–C(22), –63.5(4); N1–C1–B1–C42, 115.8(3).

B1–C1 distance of 1.612(4) Å is essentially the same as the analogous distance of 1.607(4) Å found in **6a**,^[9] but significantly shorter than that found in **5a**. Distinct bond alternation is observed throughout the borapentacene framework, with most localization of the π bonds in the outermost rings. The implications of these bond length patterns for the aromaticity associated with each ring in the conjugated framework were probed by carrying out NICS (nucleus independent chemical shift) (1) calculations on each of **6a–c** and comparing the results with those of the all-carbon analogues.^[20]

By using the X-ray structure of **6c** as a source of input coordinates, the gas-phase geometries of **6a–c** were optimized (B3LYP/6-31+G(d)). Optimized geometries for anthracene, naphthacene, and pentacene were calculated in a similar fashion. The GIAO NMR shielding tensors were then calculated by using the same functional/basis set, at ring centers (NICS(0)) and at 1 Å above the ring centers ((NICS(1)), the NICS(1)_{zz} results are shown in Figure 5.

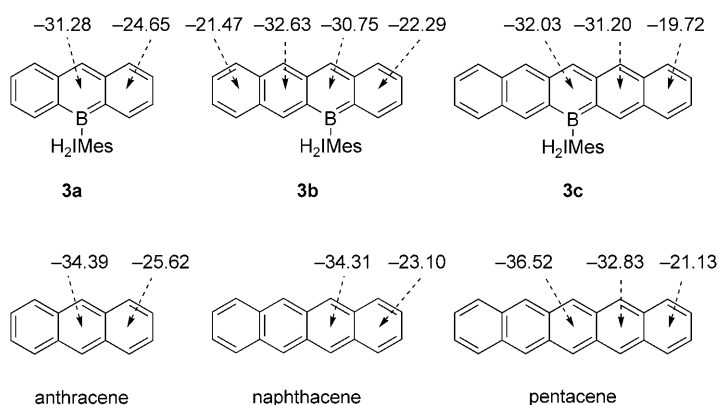


Figure 5. NICS (1)_{zz} GIAO calculations (B3LYP/6-31+G(d)) on optimized structures **6a–c** and their all-carbon counterparts anthracene, naphthacene and pentacene.^[17]

all-carbon ring of which has a NICS(1)_{zz} value of –32.63 compared with –30.75 for the adjacent boron-containing ring; both of these values are more negative than the NICS(1)_{zz} values for the outer rings (–21.47, –22.29).

In the solid state, compound **6a** is bright orange, whereas **6b** and **6c** are dark blue and green, respectively. The colors of dilute solutions are similar to those of the solids and thus, visually, the boraacenes **6a–c** appear to assume the photophysical qualities of the next highest all-carbon acenes. For example, naphthacene is an orange compound, whereas pentacene is blue; substituted hexacenes that have been isolated are green. This qualitative assessment is borne out in the photophysical and redox properties revealed in the UV/Vis–NIR spectra of **6a–c** recorded in dilute dichloromethane and compared with that of their all-carbon analogues. The combined UV/Vis–NIR absorption spectra are shown in Figure 6, while the electrochemical data is given in Table 1.

The appearance of each spectrum is broadly similar, exhibiting a sharp high-energy absorption and a broader low-energy band that has distinct fine structure. Strong bathochromic shifts are observed in the latter absorption as the boraacene framework is extended. The relatively sharp higher-energy absorption is probably associated with charge transfer from the boraacene to the NHC ligand, since the

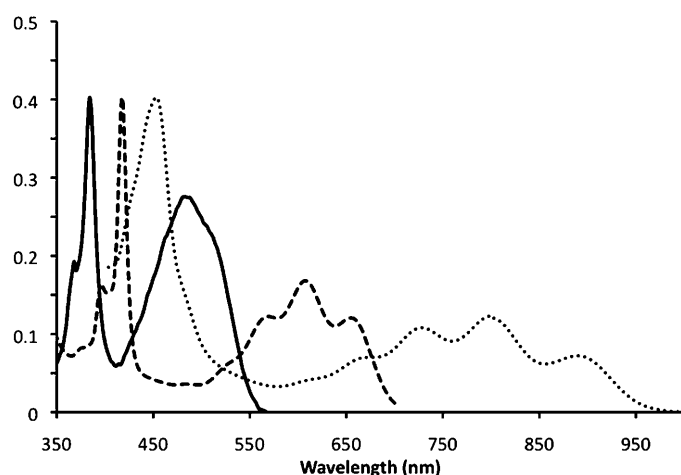


Figure 6. UV/Vis-NIR absorption spectra of boraacenes **6a** (—), **6b** (----), and **6c** (.....).

Table 1. Electrochemical summary of boraacenes **6a–c** and their all-carbon counterparts.

Compound	HOMO–LUMO [eV] ^[a]	$E_{1/2_{ox}}$ ^[b]	E.A. ^[c]	I.P. ^[d]
6a	2.25	−0.67 ^[d]	−1.0	−4.1
anthracene	3.23	0.89	−2.5	−5.7
6b	1.74	−0.66 ^[d]	−2.4	−4.1
naphthacene	2.56	0.53	−2.7	−5.3
6c	1.28	−0.91	−2.6	−3.9
pentacene	2.03	0.30	−3.1	−5.1

[a] Estimated from the onset of absorption of the wavelength UV band, CH_2Cl_2 ; [b] Test substrate 1 mm in 0.1 M $[\text{NBu}_4][\text{PF}_6]$, in CH_2Cl_2 referenced to an internal standard $\text{Fc}/\text{Fc}^+ = 0$ V, glassy carbon working electrode, Pt wire counter electrode, Ag wire pseudo reference electrode [c] E.A. = electron affinity, I.P. = ionization potential. Calculated in conjunction with optical band gap data and the placement of $\text{Fc}/\text{Fc}^+ = -4.8$ eV with respect to vacuum. [d] Irreversible (E_{ox}).

LUMO of these compounds has significant NHC character. The lower-energy band is associated with the boraacene framework and is likely due to a π – π^* transition. The peak maxima are at 485, 608, and 800 nm for **6a–c**, respectively; by comparison, the longest wavelength absorption in an NHC-stabilized borabenzene is only 306 nm.^[21] The onset of absorption for each compound is 550, 710, and 960 nm, from which HOMO–LUMO gaps of 2.25, 1.74, and 1.29 eV can be estimated. These are significantly smaller optical band gaps than the corresponding acenes; for example, that of **6b** is 0.76 eV less than that of the parent hydrocarbon naphthacene and is 0.29 eV lower than that of pentacene (2.03 eV), while that of **6c** is one of the lowest band gap non-polymeric organic materials reported. Each of these bands exhibits vibrational fine structure with peak separations of between 1150 and 1300 cm^{-1} , typical of acene “breathing” modes within the C–C framework.^[22] Compounds **6a** and **6b** were observed to be weakly fluorescent in solution and the solid phase, but **6c** exhibited no detectable fluorescence.

Electrochemical measurements on boraacenes **6a–c** and their all-carbon counterparts (Table 1) yielded estimates of the HOMO–LUMO gaps that were consistent with those

obtained from the UV/Vis spectra. Boraacenes **6a–c** were susceptible to electrochemical oxidation; for **6a** and **6b** the oxidation was irreversible, even at elevated sweep rates. In **6c**, the cyclic voltammetry (CV) trace was indicative of quasi-reversibility at higher sweep rates, suggesting that the radical cation of the extended boraacene is slightly more long-lived than those of the lower boraacenes. The compounds were not readily reduced; for **6a** any reduction process lay outside the solvent window, but for **6b** and **6c** the beginning of reduction process could be discerned just before the CH_2Cl_2 solvent window.

Conclusion

A general method for the incorporation of boron into the higher acenes has been presented. Preparation of the boracyclic precursors by transmetallation from stannacycles **3a–c** was key to the synthesis. Also important was the use of a stabilizing base that allowed for dehydrochlorination of boracycles **4** without competitive reduction.^[23] The H_2IMes NHC proved suitable for this purpose.

The H_2IMes stabilized boraacenes **6** exhibited structural properties and aromaticity patterns similar to the parent acenes within the acene framework. Photophysical and redox properties were markedly different, however. Incorporation of one boron atom into the acene framework dramatically decreases the HOMO–LUMO gap of the compounds relative to the all-carbon analogues (Figure 7) such that a given boraacene has similar properties to the next higher all-carbon acene. In general, the HOMO energy levels for boraacenes are higher in energy than the hydrocarbons due to the more electropositive nature of the boron atom within the framework, but these orbitals do not exhibit

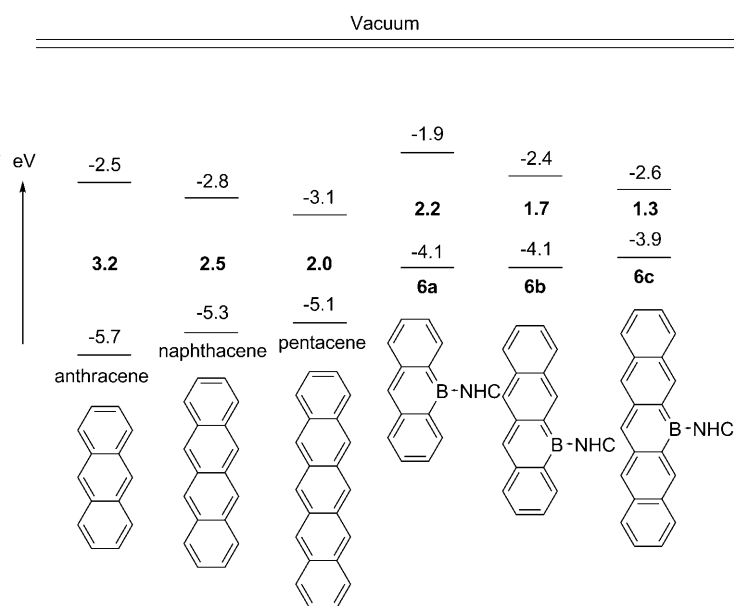


Figure 7. HOMO–LUMO levels for **6a–c** and their hydrocarbon analogues.

much variation across the **6a** to **6c** series. Rather, it is the energy of the LUMO that changes dramatically as the boracene framework is extended, since it lowers towards values closer to the all-carbon systems. This is because the effect of one boron atom becomes more diluted and the LUMO becomes more acene-like as the framework is extended. The extension of this methodology to even higher boracenes, or the preparation of polyboracenes will provide the data necessary to more conclusively delineate the effects of incorporation of boron into these important organic frameworks.

Experimental Section

General: All general methodologies are described in detail in the Supporting Information, along with descriptions of the synthesis of precursors to compounds **3**. CCDC-783463, CCDC-783464, and CCDC-783465 contains the supplementary crystallographic data for this paper, for compounds **3c**, **5a** and **6c**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of stannacycle 3a: What follows is an adaptation of the procedure initially reported by Jutzi,^[10a] including full characterization. Bis(2-bromophenyl)methane, (1.2 g, 3.7 mmol) in THF (50 mL) was added to a hot suspension of freshly activated (I_2) Mg turnings (750 mg, 30 mmol) suspended in THF (20 mL) such that the reaction maintained heat throughout the addition. Once the addition was complete the reaction was heated at reflux. Heating at reflux was continued until GCMS analysis of an aliquot quenched with HCl (6M) showed no sign of starting material. At this time the reaction was cooled to room temperature and Me_2SnCl_2 (805 mg, 3.7 mmol) dissolved in THF (12 mL) was added over 7 h by syringe pump. Once the addition was complete, the liquid was decanted, diluted with one portion of diethyl ether, and quenched with a saturated aqueous solution of ammonium chloride. The phases were separated and the aqueous layer was extracted with diethyl ether (3×30 mL). The combined organics were dried with $MgSO_4$ and concentrated in vacuo to give a viscous yellow oil. Flash chromatography (9:1 hexane/dichloromethane) gave a clear oil, which solidified upon standing (502 mg, 1.6 mmol, 45%). 1H NMR (Bruker Avance 400 MHz, $CDCl_3$): δ = 7.55 (dd, $^3J(H,H) = 7$ Hz, $^4J(H,H) = 2$ Hz, $^3J(H,^{119}Sn) = 57$ Hz, $^3J(H,^{117}Sn) = 40$ Hz, 2H; $H^{1,8}$), 7.33 (d, $^3J(H,H) = 7.2$ Hz, $^4J(H,Sn) = 22$ Hz, 2H; $H^{4,5}$), 7.19 (m, 4H; $H^{2,3,5,6}$), 3.97 (s, 2H; Ar_2CH_2), 0.53 (s, $^2J(Sn,H) = 56$ Hz, $^2J(Sn,H) = 59$ Hz, 6H; $Sn(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ = 147.1 ($J(C,^{119}Sn) = 17$ Hz, $C^{4a,10a}$), 141.1 ($C^{8a,9a}$), 136.0 ($^2J(C,Sn) = 34$ Hz, $C^{1,8}$), 128.9 ($^4J(C,^{119}Sn) = 10$ Hz, $C^{3,6}$), 128.4 ($^3J(C,^{119}Sn) = 34$ Hz, $C^{4,5}$), 126.1 ($^2J(C,^{119}Sn) = 46$ Hz, $C^{2,7}$), 46.6 ($^2J(C,^{119}Sn) = 55$ Hz, $^3J(C,^{117}Sn) = 53$ Hz, Ar_2CH_2), -10.2 ($Sn(CH_3)_2$, $^1J(C,^{119}Sn) = 370$ Hz, $^1J(C,^{117}Sn) = 353$ Hz); $^{119}Sn\{^1H\}$ NMR (148.9 MHz, $CDCl_3$): δ = -111.6 ppm; LRMS (EI): m/z (%): 316.1 (1) [M^+], 301 (67) [$M-CH_3$], 165.0 (100) [fluorenyl $^+$]; HRMS (EI): m/z calcd for $C_{15}H_{16}Sn$ [M^+]: 316.0274; found: 316.0268; elemental analysis calcd (%) for $C_{15}H_{16}Sn$: C 57.19, H 5.12, N 0; found: C 57.55, H 5.14, N -0.13.

Synthesis of boracycle 4a: Excess BCl_3 was condensed into a stirring solution of 9,10-dihydro-9,9-dimethyl-9-stannaanthracene (600 mg, 1.9 mmol) dissolved in dichloromethane (50 mL) at $-78^\circ C$. The reaction mixture was allowed to slowly come to room temperature. The volatile compounds were removed under dynamic vacuum. The resultant off-white solid was transferred to a sublimation vessel and the residual Me_2SnCl_2 was removed at ambient temperature under dynamic vacuum, leaving a grey solid (355 mg, 88%). The product is extremely moisture sensitive and should be handled accordingly. 1H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, $^3J(H,H) = 6.4$ Hz, 2H; $H^{1,8}$), 7.64 (t, $^3J(H,H) = 7.6$ Hz, 2H; $H^{3,6}$), 7.52 (d, $^3J(H,H) = 7.6$ Hz, 2H; $H^{4,5}$), 7.47 (t, $^3J(H,H) = 7.2$ Hz, 2H; $H^{2,7}$), 4.48 ppm (s, 2H; H^{10}); $^{11}B\{^1H\}$ NMR (128.2 MHz,

$CDCl_3$): δ = 55 ppm; $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 148.1 ($C^{4a,10a}$), 135.5 ($C^{1,8}$), 133.5 ($C^{3,6}$), 128.2 ($C^{4,5}$), 126.2 ppm ($C^{2,7}$); LRMS (EI): m/z (%): 212 (10) [M^+], 211 (100) [$M-H$]; LRMS (CI): m/z (%): 194 (100) [$M-Cl+NH_4$].

Synthesis of carbene adduct 5a: CH_2Cl_2 (20 mL) was condensed into a flask containing 9-bora-9-chloro-9,10-dihydroanthracene (355 mg, 1.67 mmol) and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (562 mg, 1.84 mmol) at $-78^\circ C$. Following the addition of solvent, the cold bath was removed and after stirring for 45 min the volume was reduced in vacuo and the precipitate was isolated. The crude white solid was washed with toluene and pentane followed by dichloromethane to give product of analytical purity (891 mg, 89%). 1H NMR (Bruker Avance, 400 MHz, CD_2Cl_2): δ = 6.9 (d, $^3J(H,H) = 7.2$ Hz, 2H; $H^{1,8}$), 6.83 (dd, $^3J(H,H) = 7.6$ Hz, $^4J(H,H) = 1.2$ Hz, 2H; $H^{4,5}$), 6.75 (td, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 1.2$ Hz, 2H; $H^{2,7}$), 6.61 (s, 4H; *m*-MesH), 6.43 (t, $^3J(H,H) = 7.6$ Hz, 2H; $H^{3,6}$), 3.90 (d, $^2J(H,H) = 16.4$ Hz, 1H; H^{10} , (cis to H_2 Mes)), 3.84 (s, 4H; NCH_2CH_2N), 3.55 (d, $^2J(H,H) = 16.4$ Hz, 1H; H^{10} , (cis to Cl)), 2.22 (s, 6H; *p*-Mes(CH_3)), 2.15 ppm (s, 12H; *o*-Mes(CH_3)); $^{11}B\{^1H\}$ NMR (128.2 MHz, CD_2Cl_2): δ = -6.4 ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 142.8, 138.5, 136.1, 134.8, 133.8 ($C^{4,5}$), 129.6 (*m*-MesCH), 125.7 ($C^{1,8}$), 124.6 ($C^{2,7}$), 124.5 ($C^{3,6}$), 51.6 (NCH_2CH_2N), 42.1 (CH_2), 21.1 (*p*-Mes CH_3), 18.4 ppm (*o*-Mes CH_3); LRMS (EI): m/z (%): 483 (15) [$M-HCl$], 305 (90) [H_2 Mes], 146 (100); HRMS (EI): m/z calculated for $C_{34}H_{36}^{11}BN_2Cl$ [M^+]: 518.2660; found: 518.2685; elemental analysis calcd (%) for $C_{34}H_{36}BN_2Cl$: C 78.69, H 6.99, N 5.40; found: C 78.44, H 7.16, N 5.25.

Synthesis of 9-boraanthracene 6a: 9-Bora-9-chloro-9,10-dihydroanthracene 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene adduct (640 mg, 1.23 mmol) was suspended in toluene (12 mL) and lithium tetramethylpiperidine (156 mg, 1.24 mmol) was added at ambient temperature. The mixture was stirred for 1 h at which time the orange solid was isolated by vacuum filtration and washed with toluene, followed by diethyl ether, and finally pentane. The crude solid was freed of LiCl by dissolving in dichloromethane and passing through a 0.2 μm PTFE filter (480 mg, 0.99 mmol, 80%). X-ray quality crystals were grown by cooling a supersaturated solution in bromobenzene. 1H NMR (Bruker Avance, 400 MHz, CD_2Cl_2): δ = 8.01 (d, $^3J(H,H) = 8.4$ Hz, 2H; $H^{1,8}$), 7.6 (d, $^3J(H,H) = 8.4$ Hz, 2H; $H^{4,5}$), 7.27 (s, 1H; H^{10}), 7.09 (td, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 1.3$ Hz, 2H; $H^{2,7}$), 6.75 (td, $^3J(H,H) = 6.8$ Hz, $^4J(H,H) = 1.2$ Hz, 2H; $H^{3,6}$), 6.68 (s, 4H; *m*-MesH), 4.36 (s, 4H; NCH_2CH_2N), 2.4 (s, 12H; *o*-Mes(CH_3)), 2.06 ppm (s, 6H; *p*-Mes(CH_3)); $^{11}B\{^1H\}$ NMR (128.4 MHz, CD_2Cl_2): δ = 27 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 138.9, 138.5, 135.7, 134.4 ($C^{1,8}$), 130.2 (MesCH), 128.9 ($C^{4,5}$), 124.3 ($C^{2,7}$), 115.9 ($C^{3,6}$), 113.2 (C^{10}), 52.8 (NCH_2CH_2N), 21.0 (*p*-Mes(CH_3)), 19.6 ppm (*o*-Mes(CH_3)); LRMS (EI): m/z (%): 482.5 (100) [M^+], 305.3 (74) [H_2 Mes $^+$], 177.2 (70) [$M^+ - H_2$ Mes]; HRMS (EI): m/z calc for $C_{34}H_{35}BN_2$ [M^+]: 482.2893; found: 482.2882.

Synthesis of stannacycle 3b: 2-Bromo-3-(2-bromobenzyl)naphthalene (6.2 g, 16.4 mmol) was dissolved in THF (250 mL) and slowly added to a suspension of Mg^0 (1.6 g, 65 mmol) in THF (20 mL) at reflux (activated with I_2). The rate of addition was such that the reaction remained vigorous at all times. After 1 h, GCMS analysis showed almost complete consumption of all halide-containing materials. Me_2SnCl_2 (3.6 g, 16.4 mmol) dissolved in THF (10 mL) was added over 4 h to the room temperature Grignard reagent by syringe pump. After stirring overnight the reaction was quenched with NH_4Cl (aq) and extracted with diethyl ether (3×200 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to afford the crude solid (5.84 g). The crude solid was extracted with hexane and this hexane fraction purified by flash chromatography to give the desired material (1.4 g, 23%). 1H NMR (Bruker Avance, 400 MHz, $CDCl_3$): δ = 8.07 (s, $^3J(Sn,H) = 50$ Hz, 1H; H^9), 7.82 (s, $^4J(Sn,H) = 14$ Hz, 1H; H^{11}), 7.81 (m, 2H; $H^{7,10}$), 7.61 (ddd, $^3J(Sn,H) = 47$ Hz, $^3J(H,H) = 27$ Hz, $^4J(H,H) = 1$ Hz, 1H; H^4), 7.47 (m, 2H; $H^{8,9}$), 7.44 (m, 1H; H^1), 7.31 (td, $^3J(H,H) = 7$ Hz, $^4J(H,H) = 2$ Hz, 1H; H^2), 7.26 ppm (m, 1H; H^3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 147.2 ($J(Sn,C) = 18$ Hz), 143.4 ($J(Sn,C) = 19$ Hz), 141.1, 139.7, 136.4 ($^2J(Sn,H) = 33$ Hz, C^6), 136.1 ($^2J(Sn,C) = 34$ Hz, C^4), 134.0 ($J(Sn,C) = 8$ Hz), 132.1 ($J(Sn,C) = 50$ Hz), 129.1 ($^4J(Sn,C) = 9$ Hz, C^2), 128.4 ($^2J(Sn,H) = 35$ Hz, C^1), 127.7

(C^{7/10}), 127.4 (C^{7/10}), 126.3 (C^{8/9}), 126.2 (C³), 125.7 (C¹¹), 125.6 (C^{8/9}), 46.9 (³J(Sn,C)=49 Hz, C¹²), -9.9 ppm (¹J(119Sn,C)=370, ¹J(117Sn,C)=363 Hz, Sn(CH₃)₂); ¹¹⁹Sn{¹H} NMR (149 MHz, CDCl₃): δ = -107.6; LRMS (EI): *m/z* (%): 366 (12, 8 lines) [M⁺], 351 (50, 8 lines) [M⁺-CH₃], 215 (100) [M⁺-Sn(CH₃)₂]; HRMS (EI⁺ TOF): *m/z* calcd for C₁₉H₁₈¹²⁰Sn [M⁺]: 366.0430; found: 366.0428.

Synthesis of boracycle 4b: 5,12-Dihydro-5,5-dimethyl-5-stannaphthacene (750 mg, 2.05 mmol) was dissolved in dichloromethane and cooled to -78 °C and excess BCl₃ was condensed into the reaction flask. After 30 min at this low temperature the reaction was thick with precipitate and the cold bath was removed and the reaction was allowed to warm to room temperature overnight. The volatile compounds were removed in vacuo and the residual Me₂SnCl₂ was removed by sublimation to give the desired product as a white solid (340 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ = 8.94 (s, 1H; H⁶), 8.38 (dd, ²J(H,H)=8 Hz, ³J(H,H)=1 Hz, 1H; H⁷), 8.06 (dd, ³J(H,H)=8 Hz, ⁴J(H,H)=1 Hz, 1H; H¹⁰), 7.92 (s, 1H; H¹¹), 7.87 (d, ³J(H,H)=8 Hz, 1H; H⁷), 7.62 (m, 2H; H^{3,8}), 7.54 (dm, ³J(H,H)=8 Hz, 2H; H^{1,9}), 7.47 (m, 2H; H^{9,2}), 4.61 ppm (s, 2H; H¹²); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 148.5, 141.9, 138.2 (C⁶), 136.2, 135.8 (C⁴), 134.0 (C³), 131.7, 129.9 (C¹⁰), 128.7 (C⁸), 128.3 (C¹), 127.4 (C⁷), 126.2 (C⁹), 126.0 (C¹¹), 125.8 (C²), 37.8 ppm (C¹²); ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 56.3 ppm; LRMS (EI): *m/z* (%): 262.1 (50) [M⁺], 226.1 (50) [M-HCl], 149 (100); HRMS (EI⁺ TOF): *m/z* calcd for C₁₇H₁₂¹¹BCl [M⁺]: 262.0721; found: 262.0716.

Synthesis of carbene adduct 5b: Toluene (20 mL) was condensed into a flask containing 5-bora-5-chloro-5,12-dihydronaphthacene (320 mg, 1.22 mmol) and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (448.3 mg, 1.46 mmol) at -78 °C. Following the addition of solvent, the cold bath was removed and after stirring for 45 min the volume was reduced in vacuo and the precipitate was isolated. The crude white solid was washed with toluene and pentane followed by dichloromethane to give product of analytical purity (613 mg, 89%). ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (dm, J(H,H)=7 Hz, 1H; H⁷), 7.42 (s, 1H; H⁶), 7.38 (s, 1H; H¹¹), 7.31 (m, 1H; H¹⁰), 7.18 (m, 2H; H^{8,9}), 6.95 (dm, J(H,H)=8 Hz, 1H; H¹), 6.88 (dm, J(H,H)=8 Hz, 1H; H²), 6.77 (dt, J(H,H)=7 Hz, J(H,H)=1 Hz, 1H; H³), 6.58 (s, 2H; *m*-MesH) 6.44 (tm, J(H,H)=8 Hz, 1H; H²), 6.33 (s, 2H; *m*-MesH), 4.19 (d, ²J(H,H)=16 Hz, 1H; H¹² cis to H₂IMes), 3.85 (s, 4H; NCH₂CH₂N), 3.81 (d, ²J(H,H)=16 Hz, 1H; H¹² cis to Cl), 2.23 (s, 6H; MesCH₃), 2.19 (s, 6H; MesCH₃), 2.02 ppm (s, 6H; MesCH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 142.2, 141.2, 134.2, 133.4 (C⁴), 133.2 (C⁶), 132.3, 132.1, 129.4 (*m*-MesC), 129.3, 129.1 (*m*-MesC), 128.5 (C¹⁰), 126.5 (C⁷), 125.3 (C¹), 124.6 (C³), 124.5 (C²), 124.0 (C^{8/9}), 123.4 (C^{8/9}), 122.8 (C¹¹), 51.1 (NCH₂CH₂N), 42.6 (C¹²), 20.9 (*p*-MesCH₃), 18.3 ppm (*o*-MesCH₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = -6.5; LRMS (EI): *m/z* (%): 567.8 (25) [M⁺], 532.9 (30) [M-Cl], 446.8 (28) [M-Mes], 304.9 (100) [H₂IMes]; HRMS (EI⁺ TOF): *m/z* calcd for C₃₈H₃₈¹¹BN₂Cl [M⁺]: 568.2817; found: 568.2790; elemental analysis calcd (%) for C₃₈H₃₈BN₂Cl: C 80.21, H 6.73, N 4.92; found: C 80.04, H 7.02, N 4.77.

Synthesis of 5-boranaphthacene 6b: 5-Bora-5-chloro-5,12-dihydro-6-(3-dimesityl-4,5-dihydroimidazol-2-ylidene)naphthacene (300 mg, 0.53 mmol) was suspended in toluene (20 mL) and at -78 °C LiTMP (100 mg, 0.8 mmol) dissolved in toluene was added. During the course of 1.5 h, the reaction turned from its initial color of pale yellow to blue-green to black. At this time the volume was reduced and the blue black solid was isolated by vacuum filtration. The solid was washed with hexane and dried in vacuo to afford material of spectroscopic purity (266 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (s, 1H; H⁶), 8.23 (s, 1H; H¹¹), 8.04 (d, J(H,H)=8 Hz, 1H; H⁷), 7.85 (d, J(H,H)=8 Hz, 1H; H⁷), 7.76 (d, J(H,H)=8 Hz, 1H; H¹⁰), 7.64 (d, J(H,H)=9 Hz, 1H; H¹), 7.52 (s, 1H; H¹²), 7.20 (m, 1H; H⁹), 7.15 (m, 1H; H⁸), 7.09 (m, 1H; H²), 6.70 (m, 1H; H³), 6.66 (s, 2H; *m*-MesH), 6.62 (s, 2H; *m*-MesH), 4.42 (m, 4H; NCH₂CH₂N), 2.49 (s, 6H; *o*-MesCH₃), 2.45 (s, 6H; *o*-MesCH₃), 2.01 ppm (s, 6H; *p*-MesCH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 139.1, 138.9, 137.4, 135.6, 135.5, 134.9 (C⁴), 134.4, 133.0 (C⁶), 133.5, 130.3 (*m*-MesCH), 130.1 (*m*-MesCH), 128.9 (C¹¹), 128.8 (C⁷), 128.1 (C¹⁰), 125.8, 124.9 (C²), 124.7 (C¹¹), 124.1 (C⁹), 121.7 (C⁸), 115.0 (C³), 112.3 (C¹²), 52.9 (NCH₂CH₂N), 21.0 (*p*-MesCH₃), 20.0 (*o*-MesCH₃), 19.6 ppm (*o*-MesCH₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 27.6 ppm; LRMS (EI):

m/z (%): 564 (5) [M⁺], 387.5 (20), 227.9 (100) [M-H₂IMes+H₂]; HRMS (EI⁺ TOF): *m/z* calcd for C₃₈H₃₇N₂¹¹B [M⁺]: 532.3050; found: 532.3030; elemental analysis calcd (%) for C₃₈H₃₇BN₂: C 80.85, H 6.61, N 4.96; found: C 80.11, H 7.18, N 4.80 (mix of TGT and O₂ adduct).

Synthesis of stannacycle 3c: Bis(3-bromo-naphthalen-2-yl)methane (5.4 g, 12.7 mmol) was dissolved in THF (50 mL) and added dropwise to a stirring slurry of Mg (1.85 g, mmol, activated by I₂) in THF at reflux. The rate of addition was such that the reaction maintained a steady reflux. During this time the reaction turned dark green. After 1 h, GCMS analysis of a quenched aliquot showed only one peak for debrominated starting material. The reaction mixture was further diluted with an additional THF (30 mL), cooled to room temperature, and Me₂SnCl₂ (2.93 g, mmol) dissolved in THF (40 mL) was added by slow dropwise addition. After stirring for 2 h at room temperature, the dark solution was quenched with dilute HCl and extracted with diethyl ether (3 × 50 mL) dried over Na₂SO₄ to give a tan solid (5.14 g). All of this material was extracted overnight with hexane by using Soxhlet apparatus to give Sn-containing material (1.11 g). This was further purified by flash chromatography with hexane/diethyl ether (30:1) to give reasonably pure material (1.05 g, 20%). Analytically pure material could be obtained by further flash chromatography with hexane. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (s, 2H; H^{5,7}), 7.87 (s, 2H; H^{12,14}), 7.80 (m, 4H; H^{1,4,8,11}), 7.44 (m, 4H; H^{2,3,9,10}), 4.32 (s, 2H H¹³), 0.72 ppm (m, ²J(Sn,H)=28 Hz, 6H; Sn(CH₃)₂); ¹³C NMR (50 MHz, CDCl₃): δ = 143.6 (m, ²J(Sn,H)=20 Hz, C^{12a,13a}), 139.7 (m, ¹J(119Sn,C)=445 Hz, ¹J(117Sn,C)=423 Hz, C^{5a,6a}), 136.4 (m, ²J(Sn,C)=33 Hz, C^{5,7}), 134.2 (m, ⁴J(Sn,C)=8 Hz, C^{11a,14a}), 132.1 (m, ³J(Sn,C)=50 Hz, C^{4a,7a}), 127.7 (C^{1,11}), 127.4 (C^{4,8}), 126.3 (C^{3,9}), 125.8 (m, ³J(Sn,C)=31 Hz, C^{11,14}), 125.6 (C^{2,10}), 47.26 (C¹³), -9.49 ppm (CH₃); ¹¹⁹Sn{¹H} NMR (112 MHz, CDCl₃): δ = -99.0 ppm; LRMS (EI): *m/z* (%): 415.7 (1) [M⁺], 400.9 (12) [M-CH₃], 265.1 (35), 149 (50), 45 (100); HRMS (EI): *m/z* calcd for C₂₃H₂₀¹²⁰Sn [M⁺]: 416.05870; found: 416.05987; elemental analysis calcd (%) for C₂₃H₂₀Sn: C 66.55, H 4.86, N 0; found: C 66.97, H 4.96, N -0.03.

Synthesis of boracycle 4c: Stannacycle (545 mg, 1.3 mmol) was dissolved in CH₂Cl₂ (20 mL) on a swivel frit. Excess BCl₃ gas was condensed in at -78 °C and the reaction was left to stir for 30 min at low temperature. At this time, the cold bath was removed and the reaction was allowed to slowly warm to room temperature. During this time the reaction turned grey as a precipitate became clearly visible. All volatile compounds were removed in vacuo and hexane was condensed in. Sonication resulted in a heterogeneous mixture that was separated by filtration. All solids were washed with several portions of hexane to give a grey solid. Isolation of the solid material afforded very pure product with traces of Me₂SnCl₂ (380 mg). Residual Sn impurities were removed under dynamic vacuum to give the material (350 mg, 86%). ¹H NMR (300 MHz, [D₈]THF): δ = 4.29 (s, 1H; H¹³), 7.36 (m, 4H; H^{2,3,9,10}), 7.73 (s, 2H; H^{12,14}), 7.75 (d, ³J(H,H)=7.8 Hz, 2H; H^{1,11}), 7.84 (d, ³J(H,H)=7.9 Hz, 2H; H^{4,8}), 8.43 ppm (s, 2H; H^{5,7}); ¹³C{¹H} NMR (75 MHz, [D₈]THF): δ = 41.4 (C¹³), 125.0 (C^{12,14}), 125.4, 126.3, 127.8 (C^{1,11}), 129.0 (C^{4,8}), 132.9 (C^{5,7}), 133.5, 134.8, 141.9 ppm, C^{5a,6a} were not observed; ¹¹B{¹H} NMR (128 MHz): δ = 11.1 ([D₈]THF), 53.8 ppm (CDCl₃); LRMS (EI): *m/z* (%): 312.1 (100) [M⁺], 276.0 (60) [M-Cl]; HRMS (EI): *m/z* calcd for C₂₁H₁₄BCl [M⁺]: 312.0877; found: 312.0853; elemental analysis calcd (%) for C₂₁H₁₄BCl: C 80.69, H 4.51, N 0; found: C 78.08, H 4.45, N -0.03.

Synthesis of carbene adduct 5c: CH₂Cl₂ (20 mL) was condensed into a flask containing 6-chloro-6,13-dihydro-6-bora-pentacene (493 mg, 1.6 mmol) and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (532 mg, 1.7 mmol) at -78 °C. Following the addition of solvent, the cold bath was removed and after stirring for 45 min the volume was reduced in vacuo and the precipitate was isolated. The crude white solid was washed with toluene and pentane followed by dichloromethane to give product of analytical purity (911 mg, 92%). ¹H NMR (Bruker Avance, 400 MHz, Pyridine-*d*₅): δ = 7.86 (s, 2H; H^{5,7}) 7.80 (d, ³J(H,H)=7.9 Hz, 2H; H^{4,8}), 7.62 (s, 2H; H^{12,14}), 7.45 (d, ³J(H,H)=7.8 Hz, 2H; H^{1,11}), 7.34 (m, 4H; H^{2,3,9,10}), 6.37 (s, 4H; *m*-MesH), 4.61 (d, ²J(H,H)=15.4 Hz, 1H; H¹³), 4.15 (d, ²J(H,H)=15.4 Hz, 1H; H¹³), 3.91 (s, 4H; NCH₂CH₂N), 2.35 (s, 12H; *o*-MesCH₃), 1.87 ppm (s, 6H; *p*-MesCH₃); ¹¹B{¹H} NMR (128.2 Hz, [D₅]pyridine): δ = -6.2 ppm; ¹³C{¹H} NMR (100.6 Hz,

[D₅]pyridine): δ=142.1, 138.9, 134.8, 133.9 (C^{5,7}), 133.0, 132.9, 129.5, 128.9 (C^{1,11}), 127.3 (C^{4,8}), 124.8 (C^{3,9}), 124.2 (C^{2,10}), 123.4 (C^{12,14}), 51.6 (NCH₂CH₂N), 27.2 (C¹³), 21.2 (*o*-MesCH₃), 18.6 ppm (*p*-MesCH₃); LRMS (EI): *m/z* (%): 619 (5) [M+1], 583.5 (5) [M-Cl], 305.2 (100) [H₂IMes], 276 (24) [M-H₂IMes], 264 (30) [Np-CH-Np], 146.1 (45) [mesityl aniline]; HRMS (EI): *m/z* calcd for C₄₂H₄₀¹¹BN₂³⁵Cl [M⁺]: 618.2973; found: 618.2971; elemental analysis calcd (%) for C₄₂H₄₀BN₂Cl: C 81.62, H 6.36, N 4.50; found: C 79.74, H 6.56, N 4.53.

Synthesis of 6-borapentacene 6c: Toluene (20 mL) was condensed into a flask containing 6-bora-6-chloro-6,13-dihydro-6-(3-dimesityl-4,5-dihydroimidazol-2-ylidene)pentacene (298 mg, 0.5 mmol) and at -78 °C LiTMP (73 mg, 0.6 mmol) dissolved in toluene was added and the cold bath was removed. During the course of 1.5 h, the reaction turned from its initial color of pale yellow to black. At this time the volume was reduced, the solid material was removed by filtration to give the crude material (238 mg, 79%). The mother liquor was evaporated to dryness and redissolved in a minimum amount CH₂Cl₂, filtered through a 0.2 μm PTFE syringe filter, and cooled to -35 °C to afford emerald green prisms suitable for X-ray analysis. ¹H NMR (400 MHz, CDCl₃): δ=8.75 (s, 2H; H^{5,7}), 8.30 (s, 2H; H^{12,14}), 7.86 (d, ³J(H,H)=8 Hz, 2H; H^{1,11,4,8}), 7.85 (s, 1H; H¹³), 7.77 (d, ³J(H,H)=8 Hz, 2H; H^{1,11,4,8}), 7.22 (m, 2H; H^{3,9,2,10}), 6.63 (s, 4H; NCH₂CH₂N), 2.56 (s, 12H; *o*-MesCH₃), 1.99 ppm (s, 6H; *p*-MesCH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ=39.1, 137.8, 135.6, 133.8, 130.3 (*m*-MesCH), 129.2, 124.7, 124.5, 111.5 (C13), 52.9 (NCH₂CH₂N), 20.9 (*p*-MesCH₃), 20.0 ppm (*o*-MesCH₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ=28.8 ppm; LRMS (EI): *m/z* (%): 613.1 (100) [M+O₂], 582.1 (45) [M⁺]; HRMS (EI+ TOF): calculated C₄₂H₃₉¹¹BN₂ [M⁺]: 582.3206; found: 582.3224.

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