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Synthesis of phenanthrylboroles and formal nitrene insertion to access azaborapyrenes†

Harie Zacharias,[a] Ayesha Begum,[a] Jianhua Han,[b] Tyler A. Bartholome,[a] Todd B. Marder [b] [b] and Caleb D. Martin [b] *[a]

Extended conjugation has been introduced into boroles but only on the 2,3- or 4,5-positions of the central BC_4 core. In this work we synthesize phenanthrylboroles that also have conjugation on the 3,4-positions and demonstrate their insertion reactivity with azides to furnish B,N-analogues of pyrene.

The borole core was first synthesized in 1963 by Köster and Benedikt with two fused phenyl groups as a 9-borafluorene,[1] with the monocyclic variant being prepared by Eisch and coworkers in 1969 (Fig. 1).[2] Both syntheses followed unsuccessful attempts by other teams attributed to the sensitivity of these compounds because of their four π-electron anti-aromatic state.[3] The fused phenyl groups in 9-borafluorenes diminish the anti-aromaticity as well as perturb the photophysical properties by extending conjugation.[4] There has been effort devoted to the synthesis of borole-containing polycyclic aromatic hydrocarbons (PAHs) beyond 9-borafluorene by extending conjugation with thiophene, pyrrole, furan, and pyridine heteroaromatics on the core.[5] Purely organic groups have garnered less attention with the monoaryl boraindene[6] and the binaphthyl-fused analogue 12-boradibenzofluorene being prepared.[7] In these systems, the photophysical properties of the borole are greatly influenced by the fusion of arene rings. In all borole-containing PAHs, groups have been fused to the 2,3-positions and 4,5-positions, with no examples having an arene fused at the 3,4-positions.

Boroles are effective reagents to access six-membered heteroaromatic species by the insertion of a lone pair-bearing heteroatom into the five-membered boracycle, which is thermodynamically driven by the conversion of an anti-aromatic ring to an aromatic ring.[8] This approach has been very effective to prepare 1,2-azaborine species by reaction with an azide that releases N_2 as a benign byproduct resulting in formal nitrene insertion of the α-nitrogen or, in rare cases, inserting the γ-nitrogen without N_2 extrusion.[9] The monocyclic species generally react at ambient temperature while the polycyclic variants, 9-borafluorene[10] and 12-boradibenzofluorene,[7] require heating due to their lesser degree of anti-aromaticity. Introducing a B,N isostere in place of a CC unit in PAHs also serves as a means to alter the electronic properties.[11] Thus, the preparation of new polycyclic borole frameworks presents synthetic opportunities to access B,N-containing PAHs. In this work, we disclose a borole that features a phenanthryl backbone to introduce conjugation extending along the three C–C linkages in boroles and investigate its nitrene insertion reactivity to target a B,N-containing pyrene.

Boron/tin transmetalation is an effective method to prepare borole species.[12] A stannole featuring methyl groups on tin and a phenanthryl backbone (1) was prepared by treating 4,5-diiodophenanthrene with 2.1 equivalents of nBuLi and reaction with Me_2SnCl_2 (Fig. 2a). The ^1H NMR spectrum features a methyl resonance at 0.64 ppm with diagnostic satellites from coupling to the NMR active isotopes of tin ($^2J_{Sn-H}$ = 32 Hz). Reactions of 1 with BCl_3 and $PhBCl_2$ in $CDCl_3$ were monitored by *in situ* ^{11}B and ^1H NMR spectroscopy with no reaction occurring at 23 °C after 3 days. Heating to 75 °C resulted in new ^{11}B signals emerging at 63.3 and 63.1 ppm for the reactions with BCl_3 and $PhBCl_2$, respectively, with complete

[a] *Department of Chemistry and Biochemistry, Baylor University, One Bear Place #97348, Waco, Texas 76798, USA.*
E-mail: caleb_d_martin@baylor.edu

[b] *Institut für Anorganische Chemie, and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

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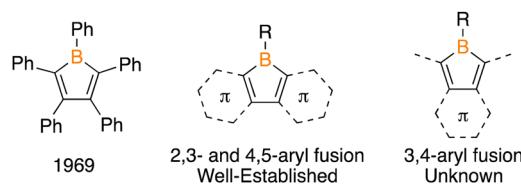

Fig. 1 Monocyclic borole, general structure of known aryl-fused variants, and the unknown 3,4-aryl fused variant.

consumption of both the borane reagent and **1** after 48 hours. The [11]B resonances are in the region of those reported for 9-borafluorenes.[4a,b] Upon workup, the products were isolated and, from the reaction with BCl_3, we were able to grow single crystals suitable for X-ray diffraction confirming the structure of the phenanthryl borole **2Cl** (Fig. 2b). Comparing the metrical parameters of **2Cl** to 9-Cl-9-borafluorene,[13] a notable difference is a shorter C2–C3 bond in **2Cl** [1.431(8) Å] versus that in 9-Cl-9-borafluorene [1.481(3) Å], attributed to the C2–C3 bond being within an aromatic ring in **2Cl** (see ESI,† Table S2). In the ^{1}H NMR spectrum of **2Cl**, four resonances are observed, each integrating to two, consistent with the symmetric structure of a phenanthrylborole. The corresponding ^{1}H NMR spectrum of **2Ph** displays the same pattern of four aryl signals, but also shows signals for the five phenyl hydrogen atoms.

To assess the Lewis acidity and propensity for insertion reactivity, Gutmann–Beckett acceptor numbers (AN) for **2Cl** and **2Ph** in C_6D_6 were determined to be 80.3 and 77.6, respectively. Comparing the values to the related 9-borafluorene compounds with the same substitution reveals an enhancement of Lewis acidity in the phenanthryl over the biphenyl compounds with the same trend of the chloro species being more Lewis acidic than the phenyl analogue (9-Cl-9-borafluorene = 78.7, 9-Ph-9-borafluorene = 73.4).[10a] The value for **2Ph** is less than that of pentaphenylborole (79.2), but the value of a monocyclic chloroborole has not been reported. Given that 9-Cl-9-borafluorene and 9-Ph-9-borafluorene undergo insertion,[14] this suggests that phenanthrylboroles **2Cl** and **2Ph** should be poised for such reactivity.

With **2Cl** and **2Ph** in hand, we targeted the insertion of an azide to access B,N-containing analogues of pyrene. In examining the literature, one article on 1,2-species was published by

Dewar and coworkers in 1964.[15] Their synthetic strategy was a dehydrohalogenative coupling reaction of an amino phenanthrene with a chloroborane that underwent an intramolecular cyclization to furnish the B,N-pyrene. Other groups have prepared different isomers,[16] but Dewar's work is the only report of a B,N pyrene with this connectivity.[15] We felt our method could furnish the species akin to Dewar's compounds.

Treatment of **2Cl** and **2Ph** with benzyl azide ($PhCH_2N_3$) at 23 °C resulted in the immediate formation of bubbles consistent with N_2 evolution and a loss of the yellow colour to give a colourless solution. Analyzing the reactions by in situ ^{11}B NMR spectroscopy revealed upfield shifts from **2Cl** and **2Ph** within 15 min (**2Cl**: 63.3 to 37.1 ppm; **2Ph**: 63.1 to 29.5 ppm). A break in symmetry of the aryl resonances in the ^{1}H NMR on the phenanthrene backbone for both species is consistent with a formal nitrene insertion. The methylene hydrogens derived from the benzyl azide were observed at 5.52 and 5.43 ppm, for the reactions with **2Ph** and **2Cl**, respectively. The structure of the chloro species was confirmed to be the desired BN-pyrene by a single crystal X-ray diffraction study (Fig. 2). Compound **3Ph** is sufficiently stable for purification by flash column chromatography on silica gel, while **3Cl** is moisture sensitive.[17]

Examining the metrical parameters of **3Cl** and comparing them to the structures of 9,10-B,N-phenanthrenes[10,18] revealed analogous parameters within the tricyclic framework (see ESI,† Table S3). The C2–C3 bond length is similar [1.473(3) Å vs. 1.469(3) Å] and lengthened from the borole precursor [**2Cl** = 1.431(8) Å]. The B–N bond distance [1.406(3) Å] is expectedly longer than the C–C bond length of pyrene [1.344(2) Å][19] and shorter than the B–N bond of the internal BN-pyrene reported by Piers and coworkers [1.456(4) Å].[16a]
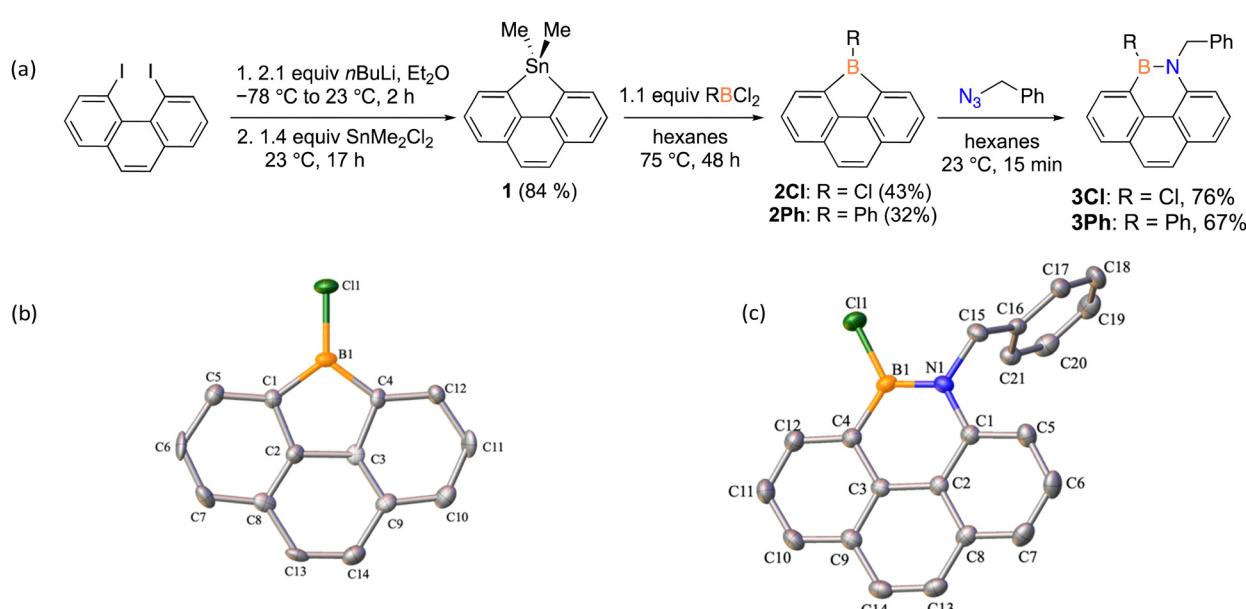

Fig. 2 (a) Synthesis of phenanthrylboroles **2Cl** and **2Ph**. (b) Solid-state structure of **2Cl**. (c) Solid-state structure of **3Cl**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) for **2Cl**: B(1)−Cl(1) 1.746(8), B(1)−C(1) 1.580(1), C(1)−C(2) 1.417(9), C(2)−C(3) 1.431(8), C(3)−C(4) 1.444(10), B(1)−C(4) 1.541(10); for **3Cl**: B(1)−Cl(1) 1.789(3), B(1)−N(1) 1.406(3), N(1)−C(1) 1.418(3), C(1)−C(2) 1.424(3), C(2)−C(3) 1.434(3), C(3)−C(4) 1.422(3), C(4)−B(1) 1.540(4).

Table 1 Photophysical data of the compounds in CH_2Cl_2

Compound	λ_{abs} [nm] (ε [10^4 M^{-1} cm^{-1}])	$\lambda_{em}{}^a$ [nm]	Stokes shift [cm^{-1}]	φ_f	τ [ns]	$k_r{}^b$ [10^7 s^{-1}]	$k_{nr}{}^b$ [10^7 s^{-1}]
2Ph	254 (2.0)	365, 375	c	22%	13.1	1.7	6.0
3Cl	254 (5.2), 370 (0.6)	375, 393	360	21%	4.5	4.7	17.6
3Ph	253 (6.9), 370 (1.3)	375, 393	360	27%	4.5	6.0	16.2

^{a} Excited at 254 nm. ^{b} The non-radiative rate constants (k_{nr}) were calculated from $k_{nr} = (1 - \varphi_f)/\tau$. The radiative rate constants (k_r) were calculated from $k_r = \varphi_f/\tau$. ^{c} As there may well be a very weak and broad absorption around 350 nm, it is likely not appropriate to use the 254 nm absorption to calculate a Stokes shift.
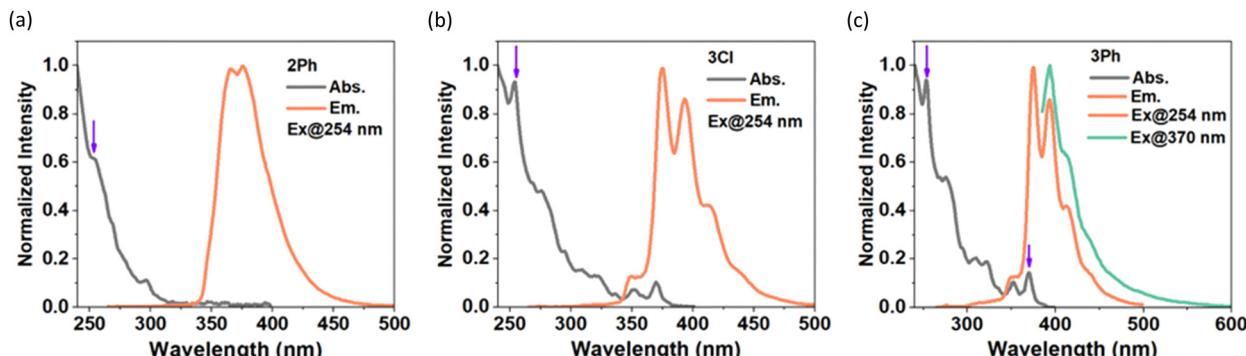
Fig. 3 Absorption and emission spectra of (a) **2Ph**, (b) **3Cl**, and (c) **3Ph** in CH_2Cl_2 ($< 10^{-5}$ M). The linear dependence of absorbance on concentration is presented in Fig. S23 (ESI†), and excitation spectra are provided in Fig. S24 (ESI†).

The photophysical properties of **2Ph**, **3Cl**, and **3Ph** were examined by UV/Vis and fluorescence spectroscopy (Table 1, Fig. 3); however, compound **2Cl** was too sensitive to handle at the requisite low concentrations for these studies. The absorption spectra feature strong bands in the UV region (253–373 nm); excitation in CH_2Cl_2 resulted in emission at $\lambda_{em} = 365$–393 nm, with modest quantum yields ($\varphi_f = 0.21$–0.27) and short lifetimes ($\tau = 4.5$–13.1 ns; Table 1) compared to that of pyrene.[20] Compound **2Ph** exhibits absorption maxima at 254 nm and 297 nm and emission maxima at 365 nm and 375 nm with a quantum yield of 0.22. It is possible that there is an extremely weak and broad absorption around 350 nm, but this remains difficult to discern even at higher concentrations. The absorption maxima of **3Cl** and **3Ph** are identical to one another, with peaks at 254 nm and 370 nm, significantly blue-shifted compared to those of the internal BN-pyrene reported by Piers and coworkers,[16a] but consistent with the absorption data (e.g., $\lambda_{abs} = 365$ nm) reported by Dewar and coworkers for the parent '5,4-borazaropyrene' as they referred to the BHNH-containing analogue of our compounds of type **3**, and the extremely weak $S_1 \leftarrow S_0$ transition ($\lambda_{abs} = 362$ nm in toluene, and 372 nm in cyclohexane) for pyrene itself. The emission spectra of **3Cl** and **3Ph** exhibit very small Stokes shifts (360 cm^{-1}) consistent with those of classic pyrene derivatives, indicating small changes in geometry between the ground and excited states,[20] with emission maxima showing clear vibrational bands at 375 nm and 393 nm, and shoulders at lower energy (cf. λ_{em} of pyrene = 372 nm in toluene); moderate quantum yields of 0.21 and 0.27, respectively, are observed.

In summary, we have established synthetic routes for two types of tetracyclic boron heterocycles, the first being boroles featuring a phenanthrene framework that represent the first of the borole family featuring aryl fusion on the 3,4-positions of the central BC_4 core. Reaction of the fused borole with benzyl azide furnishes a pyrene analogue with a BN unit in place of one of the CC bonds. The reactivity disclosed diversifies the chemicals space in the fields of boroles, pyrenes, and boron-containing polycyclic aromatic hydrocarbons as a whole.

Data availability

The data underlying this study are available in the published article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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