# Redox- and Charge-State Dependent Trends in 5, 6, and 7-Membered Boron Heterocycles: A Neutral Ligand Coordination Chemistry Approach to Boracyclic Cations, Anions, and Radicals

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## CONSPECTUS

Boron heterocycles have emerged as an important subset of heteroatom-incorporated rings, attracting substantial attention from organic, inorganic, and materials chemists. The empty $p_z$ orbital at the boron center make them standout as quintessential Lewis acidic molecules, also serving as means to modulate electronic structure and photophysical properties in a facile manner. As boracycles are ripe for extensive functionalization, they have found use in catalysis, chemical biology, materials science, and continue to be explored as chemical synthons for conjugated materials and reagents. Neutral boron(III)-incorporated polycyclic molecules represent some of the most studied types of boracycles, and understanding their redox transformations are important for applications which rely on electron transfer and charge transport. While relevant redox species can often be electrochemically observed, it remains challenging to isolate and characterize boracycles where the boron center and/or polycyclic skeleton have been chemically reduced.

This Account describes our recent work on the isolation of 5-, 6-, and 7-membered boracyclic radicals, anions, and cations, with special attention being dedicated to stabilization strategies, ligand-mediated bonding situations, and reactivity. We present a versatile neutral ligand coordination chemistry approach which allows one to transform the character of boracycles from potent electrophiles, to powerful nucleophilic heterocycles, that facilitate diverse electron transfer and bond activation chemistry. Although there are a wide range of suitable stabilizing ligands, we have employed both diamino-N-heterocyclic carbenes (NHCs) and cyclic(alkyl)(amino) carbenes (CAACs), which led to boracycles with tunable electronic structures and aromaticity trends. We highlight the successful isolation of borafluorene radicals and demonstrate their reversible redox behavior, undergoing oxidation to the cation or reduction to the anion. The borafluorene anion is a versatile chemical synthon and has been used to prepare boryl-main-group and transition-metal bonds, luminescent oxabora-spirocycles, borafluorenate-crown ethers, and CO-releasing molecules via carbon dioxide activation. We expanded our work to 6-membered boracycles and characterized neutral bis(NHC-supported 9-boraphenanthrene)s and the corresponding bis(CAAC-stabilized 9-boraphenanthrene) biradical. The choice of ligand (diamino-NHC versus CAAC) dictates the formation of bis(9-boraphenanthrene) closed- or open-shell molecules, highlighting ligand-mediated strategies for the formation of π-electron-rich boracycles in specific electronic states. The red-emissive neutral bis(boraphenanthrene)s exhibit dual-emission in solution as a result of excited state conjugation enhancement. We also detail the interconvertible multi-redox states of boraphenalene, where the boraphenalenyl radical, anion, and cation mimic

the charge-states of the all-hydrocarbon analogue. Reactivity studies of the boraphenalenyl anion displayed unusual nucleophilic reactivity at multiple sites on the periphery of boraphenalenyl tricyclic scaffold. Reduced borepins, 7-membered boron containing heterocycles, have also been isolated. We used a stepwise one-pot synthesis combining the halo-borepin precursor, CAAC, and $KC_8$ to afford the monomeric borepin radicals and anions. The π-system was extended to contain two borepin rings fused together in a pentacyclic scaffold, which permitted the isolation of diborepin biradicals and a diborepin containing a dibora-quinone core. Trends in the reactivity of the biradicals were uncovered based on the localization of electron density around boron and % biradical character, enabling oxidation to a bis(borepin hydride) or reduction to a bis(borepin anion).

Our goal for this Account is to provide a guide which explains the current structure-function trends and isolation strategies for redox-active boron-incorporated polycyclic molecules, to initiate the rational design and use of these types of compounds across a vast chemical space.

## KEY REFERENCES

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- Sarkar, S. K., Hollister, K. K., Molino, A., Obi, A. D., Deng, C.-L., Tra, B. Y. E., Stewart, B. M., Dickie, D. A., Wilson, D. J. D.,* Gilliard, R. J., Jr.,* Bis(9-Boraphenanthrene) and Its Stable Biradical. *J. Am. Chem. Soc.* **2023**, 145, 21475-21482.[2] *Red to near-infrared-emissive neutral bis(9-boraphenanthrene)s were prepared, which exhibit dual-emission due to an excited state conjugation enhancement mechanism. A bis(9-boraphenanthrene) open-shell singlet biradical was also structurally confirmed for the first time, which contained high biradical character at 95%.*
- Hollister, K. K., Molino, A., Jones, N., Le. V. V., Dickie, D. A., Cafiso, D. S., Wilson, D. J. D.,* Gilliard, R. J., Jr.* Unlocking Biradical Character in Diborepins. *J. Am. Chem. Soc.* **2024**, 146, 6506-6515.[3] *Borepin biradicals were synthesized, containing an open-shell singlet ground-state and thermally accessible triplet-state. A strategy was revealed to modulate biradical character based on the bending of the pentacyclic framework, affording a closed-shell dibora-quinone core in the doubly-reduced planar diborepin system.*
- Deng, C.-L., Hollister, K. K, Molino, A., Tra, B. Y. E., Dickie, D. A., Wilson, D. J. D., Gilliard, R. J., Jr.* Unveiling Three Interconvertible Redox States of Boraphenalene. *J. Am. Chem. Soc.* **2024**, 146, 6145-6156.[4] *New charge and redox states were introduced for boraphenalene, showing reversible interconvertibility between the boraphenalenyl cation, radical, and anion. The reactivity of reduced boraphenalenyls were delineated, where the anion permits the formation of substituted boraphenalenyls and C–C coupling products.*

## INTRODUCTION

Developing the synthesis, reactivity, and applications of organoboron compounds has been a central tenet of synthetic chemistry disciplines for decades. These molecules have wide-ranging applications in chemical biology, catalysis, materials science and engineering, and have been the subject of fundamental investigations into structure and bonding from both organic and inorganic chemistry perspectives.[5] An area of boron chemistry that continues to see increasing interest is the chemistry of boron-containing rings, or boracycles. When tricoordinate boron is placed in specific positions of cyclic molecules, it provides a Lewis acidic site for facile electronic structure tuning.[5a] The majority of boron heterocycles that have been isolated and characterized feature the boron atom clearly in the B(III) oxidation state.[5d] However, our laboratory and others have begun to isolate and structurally authenticate relatively rare examples of boron-doped polycyclic aromatic hydrocarbons (B-PAH) where the boron atom and/or PAH skeleton have been chemically reduced.[6] In doing so, we have discovered trends in the function of boracycles based on their specific redox-state. While we have reported a number of relevant B-PAHs,[7] this Account will focus on the chemistry of redox-active borafluorenes, boraphenanthrenes, boraphenalenes, and borepins.

En route to synthesizing reduced boracycles, we have employed a neutral ligand-coordination approach (Figure 1), whereby Lewis acidic B-PAHs, containing a vacant $p_z$ orbital at the tricoordinate boron center, undergo coordination by a Lewis base (e.g., phosphine, carbene, amine). The resulting tetracoordinate boracycles serve as molecular precursors for B-PAH cations, radicals, and anions. Even within specific redox- and charge-states, it is possible to drastically alter the electrophilic or nucleophilic character of a boracycle by changing the functional groups on the ligand and/or PAH. Thus, this strategy serves as a versatile method to control the stability, aromaticity, redox potentials, chemical reactivity, and photophysical properties of boracyclic molecules.

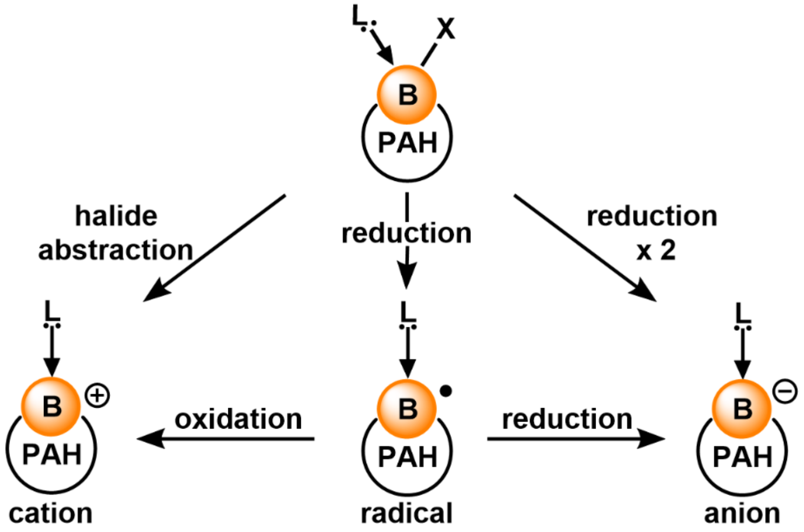


**Figure 1.** Overview of neutral ligand strategy toward boracycles in distinct redox- and charge-states.

As boracycles are reduced, the electron-richness at the boron center increases, transforming inherently electrophilic molecules into powerful nucleophiles.[6a, c, d, f, h, 8] Consequently, these types of molecules are often extremely reactive and difficult to isolate. However, isolable radicals and anions can be realized with appropriate ligand design strategies, whereby electronic and steric factors significantly influence the ground state electronic structure. While there are countless neutral donor ligands known, our ligand of choice in most cases has been carbenes. These are neutral two-electron donor ligands, which have been employed to stabilize numerous transition metal and main-group species.[9] Diamino-N-heterocyclic carbenes (NHCs)[10] and cyclic(alkyl)(amino) carbenes (CAACs)[11] are both strong σ-donors, but CAACs have more π-accepting character than NHCs,[9] resulting in drastically different bonding modes between the boron atom and carbene. In the types of carbene-B-PAH molecules that we have isolated, the electrons that result from reduction can be boron localized or delocalized onto the ligand and/or PAH. Understanding the location and degree of delocalization is critical for the development of applications which depend on redox processes (e.g., organic light emitting diodes, organic field-effect transistors).[5g] In addition, while the boron-adjacent atom is typically carbon, boracycles can be prepared which contain heteroatoms, providing an additional site for structure-function tuning.[7a, 12] Thus, we suggest that this strategy will continue to permit the generation of unprecedented boracycles which are either inaccessible by other means or simply unexplored, opening the door to new applications.

## 2. Reduced 5-Membered Boracycles: Borafluorenes

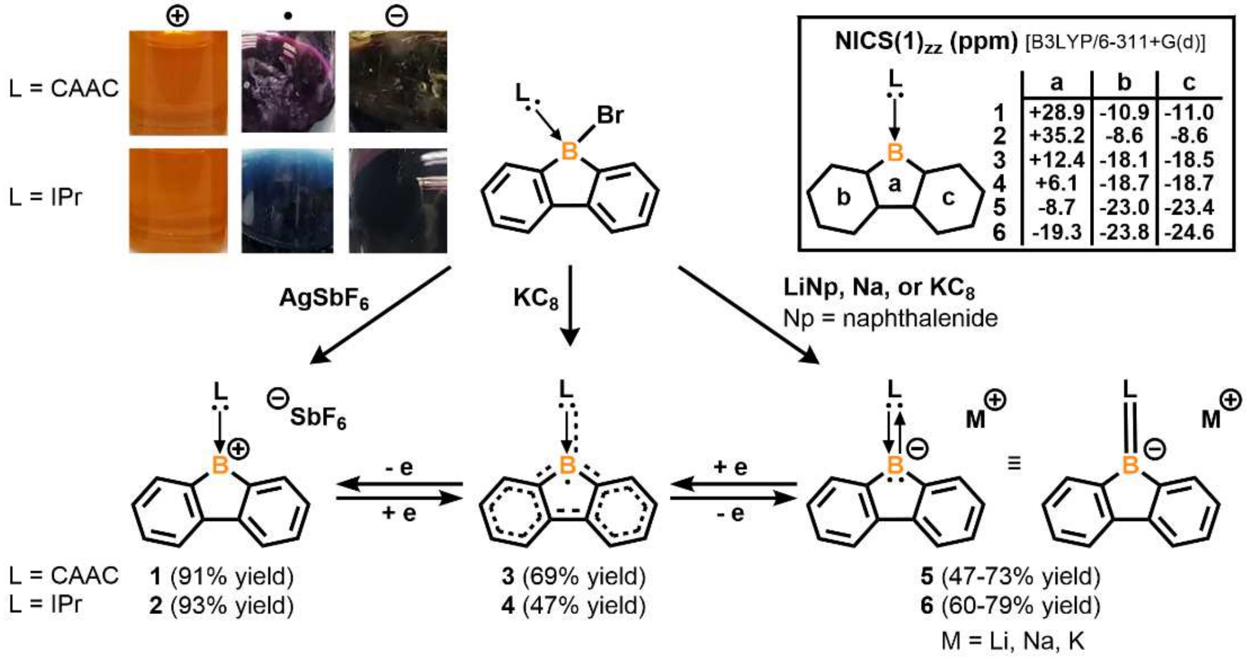
9-borafluorene (BF), a tricyclic scaffold containing a central 5-membered boron-doped ring fused with two phenyl groups, is an analogue of the all-hydrocarbon fluorenyl cation.[13] Borafluorenes have been investigated for a variety of fundamental and applied pursuits, including bond activation, molecular sensing, nonlinear optical switches, catalyst initiators, and solar cells.[13] Although they were first synthesized in the 1960s,[14] it was not until the 21st century that scientists documented attempts to chemically reduce them. Rivard added two equivalents of $KC_8$ to a 9-NHC-9-chloro-borafluorene complex, targeting the NHC-borafluorene monoanion; however, they isolated a hydrido-borafluorene via hydrogen abstraction from the reaction solvent or protonation due to residual water.[15] Therefore, it was concluded that NHC-stabilization was an insufficient method to permit the isolation of these types of compounds. Borafluorene dianions were also isolated by Wagner through two-electron reduction of 9-*H*-9-borafluorene and tetraanions via the addition of excess reducing agent to 9-methoxy-9-borafluorene.[16]

### 2.1 Synthesis of Borafluorene Radicals and Anions

In the intervening years, we began to synthesize cations across the s- and p-blocks of the periodic table and reported that halide abstraction of tetracoordinate halo-borafluorene results in the formation of borafluorenium ions **1** and **2** (Scheme 1).[17] While the optical properties of borafluorene cations will not be discussed, we have found them to be viable thermochromic[17] and thermoluminescent[18] molecular materials. With the 9-CAAC-9-borafluorene cation [CAAC = 2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethyl-pyrrolidin-5-ylidene] and its halide precursors in hand,[15] this presented an opportunity to investigate the isolation of borafluorene radicals. After adding one equivalent of $KC_8$ to the 9-CAAC-9-borafluorenes, an immediate color change was observed and the CAAC-stabilized borafluorene radical **3** was isolated.[19] Compound **3** was stable under inert atmosphere and thus we sought to compare it with the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) NHC analogue, which was undoubtedly an unexplored intermediate in the Rivard synthesis. Surprisingly, the NHC-borafluorene radical **4** was also isolated, albeit in lower crystalline yield. A comparison of the two species demonstrates the impact of ligand choice on the delocalization of the unpaired spin. With its greater affinity for accepting π-electrons, **3** has 0.38 $e^-$ net spin density on the ligand whereas **4** has only 0.16 $e^-$. However, both radicals possess greater than 50% spin density on the B-PAH with the highest percentage being on boron (**3**: 32%; **4**: 37%).

When carrying out cyclic voltammetry studies on these radicals, we observed reversible reduction waves which indicated that under certain conditions the two-electron reduced 9-carbene-9-borafluorene monoanions should be isolable. While the oxidation appears to be irreversible in the reported spectra, this is only due to THF coordination to the cation.[17] Due to the reported challenges associated with reduction of the NHC-coordinated 9-bromo-9-borafluorene,[15] we sought to isolate a borafluorene monoanion starting from our CAAC-coordinated 9-bromo-9-borafluorene.[17] The hypothesis was that with CAACs superior π-accepting ability, added electron density would partially delocalize onto the ligand, lessening the concentrated electron-richness at the boron center and increasing its stability. The addition of lithium naphthalenide (LiNp), sodium metal (Na), or potassium graphite ($KC_8$) to a solution of 9-CAAC-9-borafluorene immediately resulted in purple solutions consistent with the formation of the borafluorene radical intermediate. After vigorous stirring at room temperature overnight, deep red solutions were observed, and the corresponding CAAC-borafluorene monoanions (**5**) were isolated as red solids.[1] The stability and long shelf-life of **5** merited revisiting the NHC analogues. Under extremely rigorous air- and moisture-free conditions, the corresponding NHC-borafluorene monoanions **6** were isolated as indigo solids and crystallographically characterized; however, they were significantly less stable in solution and convert to the NHC-hydrido-borafluorene. The improved stability of **5** can be tied to the π-accepting ability of CAAC, which results in a polarized $B{=}C^{carbene}$ bond.

**Scheme 1. Synthesis of borafluorene cations (1,2), radicals (3,4), and anions (5,6).**



|  | a | b | c |
|---|---|---|---|
| 1 | +28.9 | -10.9 | -11.0 |
| 2 | +35.2 | -8.6 | -8.6 |
| 3 | +12.4 | -18.1 | -18.5 |
| 4 | +6.1 | -18.7 | -18.7 |
| 5 | -8.7 | -23.0 | -23.4 |
| 6 | -19.3 | -23.8 | -24.6 |

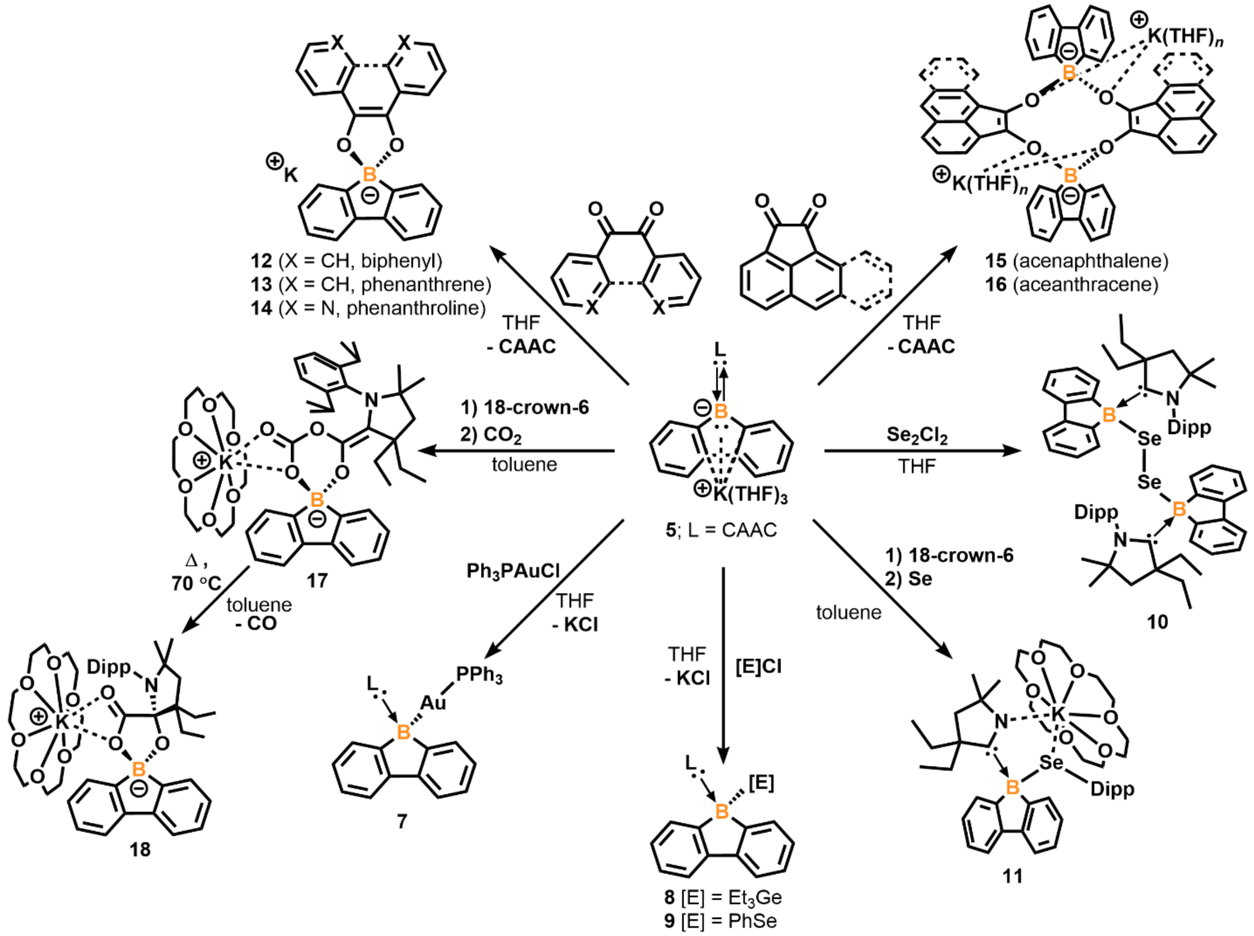
In **3** and **4**, the solid arrow from the ligand depicts two-electron donation to boron, while the dashed lines represent delocalization of the radical on borafluorene and the ligand. The solid arrows in **5** and **6** indicate the coupling of the two electrons donated from the ligand, and the back-donation of the two electrons at the boron center, forming a polarized C=B double bond. Back-donation is comparatively less prominent in NHC-coordinated boracycles.

Compounds **5** and **6** (M = Li, Na, K) were characterized by NMR spectroscopy and single-crystal X-ray diffraction. The potassium analogues were the easiest to isolate and displayed contacts between the electron-rich boron and solvated countercation. When [CAAC-BF][K(THF)$_3$] is combined with 18-crown-6, 2.2.2-cryptand, or 9,10-phenanthroline, all cation contacts are eliminated and charge-separated ion pairs are obtained.[20] These charge-separated ion pairs are characterized by downfield $^{11}$B{$^1$H} NMR chemical shifts at 14.2-15.4 ppm which differ from [CAAC-BF][K(THF)$_3$] at 1.5 ppm. Computations suggest that increasing the distance between the borafluorene anion and countercation increases the nucleophilicity of the complex, and therefore the reactivity can be controlled by modulating the charge separation. NICS(1) calculations indicate that the borole ring progresses from anti-aromatic (**1**, **2**) to non-aromatic (**3**, **4**) to aromatic (**5**, **6**) as more electrons are added, while the outer benzene rings retain aromaticity in **1**-**6** (Scheme 1).

## 2.2 Reactivity of Tricoordinate Borafluorene Monoanions

In an effort to explore the chemical reactivity of the 9-carbene-9-borafluorene monoanions, we have tested reactions with various substrates (Scheme 2). [CAAC-BF][K(THF)$_3$] (**5**) was selected for reactivity studies as it can be prepared on multi-gram scales and stored in the glovebox for months. Reacting **5** (M=K) with transition metal and main-group halides ($Ph_3PAuCl$, $Et_3GeCl$, PhSeCl) eliminated KCl and generated tetracoordinate borafluorenes containing B–Au (**7**), B–Ge (**8**), and B–Se (**9**) bonds.[1] Reactions were also attempted using the NHC-BF anion **6**, however, the NHC-hydrido-borafluorene was often the major product and thus **5** remains the most viable chemical synthon.

**Scheme 2. Reactivity of [CAAC-BF][K(THF)$_3$] (5)**



Compound **5** also reacts with $Se_2Cl_2$ to produce the boryl-substituted diselenide **10** via salt elimination.[21] Initial reactions between **5** and grey selenium led to a mixture of five different borafluorene- and selenium-containing products, characterized from a single reaction via NMR and X-ray crystallography.[21] In an effort to increase selectivity, 18-crown-6 was added to **5** and reacted with grey selenium, which yielded the boryl-substituted selenide **11** as the sole product. The reaction between **5** and selenium was calculated to proceed via single-electron transfer (SET) and experimental support for this mechanism was demonstrated through a reaction with radical **3** and selenium dichloride, which also produced **10**.

In the presence of 9,10-phenanthrenequinone or 1,10-phenanthroline-5,6-dione, **5** loses CAAC to form fluorescent spirocycles **12-14**, respectively.[20] Alternatively, when non-benzenoid quinones are employed, 10-membered dianionic tetraoxaboracycles **15** and **16** are formed (i.e., crown ethers featuring borafluorenate units).[22] Upon the reaction with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$), boracycle **15** exchanges one $K^+$ for $Na^+$, which strongly binds to the cavity of the crown through four oxygen atoms. Theoretical modeling suggests that the formation of **15** and **16** is restricted to non-benzenoid quinones due to the lower electronic stability of the respective boron intermediates (see original report for a discussion of the reaction mechanism).[22]

Consistent with its electron-rich nature, compound **5** serves as a nucleophile for the activation of carbon dioxide and the trioxaborinanone **17** was isolated.[23] Exposing **17** to broadband UV light, or heating to 70 °C, results in the formation of the blue-fluorescent dioxaborinanone **18** via the release of carbon monoxide. These reactivity studies highlight the unique ability of borafluorene monoanions to react via both nucleophilic substitution and SET mechanisms. Despite the reduced borafluorenes being air-sensitive, they have led to an array of air-stable products and can serve as valuable chemical synthons.

## 3. Reduced 6-Membered Boracycles: Boraphenanthrenes and Boraphenalenes

As the most critical building block in organic chemistry, researchers have devoted significant efforts towards modifying and tuning the aromaticity of benzene rings. We became interested in phenanthrene due to its inherent stability and luminescent properties, which have been valuable for molecular materials and photoredox chemistry.[24] Derivatives of phenanthrene have also found use in medicinal chemistry for their anticancer, anti-inflammatory, and antibacterial properties.[25] Researchers have found ways to incorporate various heteroatoms (i.e., N, P, S) into the phenanthrene scaffold, primarily as a means to develop conjugated materials with distinct properties.[26] There are reports of BN-phenanthrenes,[27] boroxophenanthrene,[28] and our lab reported a neutral BP-phenanthryne through photolysis of a boraphosphaketene.[22] Martin and coworkers isolated the first 9-borataphenanthrene anion and explored its reactivity.[29] We noted that the neutral and radical forms of boraphenanthrene had not been reported but would provide useful building blocks for more complex benzene-rich molecular scaffolds that contain boron.

### 3.1 Synthesis of Neutral Bis(9-Boraphenanthrene) and its Biradical

Combining two equivalents of 9-chloro-9-borafluorene and 1,4-bis((trimethylsilyl)ethynyl)benzene at room temperature, we initially expected to isolate the *b*,*d*-borepin ring expansion product, similar to work published by Fukushima.[30] Instead, we observed ring expansion to the six-membered 9-boraphenanthrene and migration of the trimethylsilyl group to form **19** as a yellow solid (Figure 2).[2] This unique ring expansion is likely promoted by the silyl group, although more detailed mechanistic studies are needed to determine why other substituents on the alkyne result in ring expansion to the 7-membered ring. Due to the trimethylsilyl groups, sterically demanding Lewis-bases do not coordinate to **19**; therefore, a one-pot reduction and ligand coordination strategy was employed to isolate the reduced species. Compound **19** and $KC_8$ were added together in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($I^iPr_2$), 1,3,4,5-tetramethylimidazol-2-ylidene ($IMe_4$), or CAAC in a 1:2:2 ratio to isolate compounds **20-22** (Figure 2). Compounds **20** and **21** displayed resolved $^1$H NMR signals indicating closed-shell molecules, whereas **22** showed broad resonances indicative of a paramagnetic species.

Single-crystal X-ray diffraction studies were performed on **19-22**, and all compounds show the boron atoms slightly bent out of the plane of the 6-membered ring due to steric hinderance with the $SiMe_3$ groups. Compounds **20** and **21** displayed bond distances consistent with a double bond between the endocyclic B–C bonds [**20**: 1.469(4) Å; **21**: 1.467(4) Å], resulting in a fully aromatized boraphenanthrene ring. Comparatively, the same endocyclic B–C bond is significantly longer [1.619(4) Å] in **22** and is consistent with single bond character. The exocyclic $^{carbene}$C–B bonds in **20** [1.604(3) Å] and **21** [1.604(3) Å] are slightly longer than in **22** [1.545(5) Å]. These data suggested the closed-shell resonance form for **20** and **21** and the open-shell biradical for **22**. Variable temperature EPR data displayed a temperature dependence on the $m_s = \pm1$ transition and observance of the $m_s = 2$ transition at low temperature, indicative of a triplet species. Theoretical calculations (B3LYP-D3(BJ)/def2-TZVP with DLPNO-NEVPT2 and CASSCF(2,2)/def2-TZVP) indicated an open-shell singlet ground state with a small singlet-triplet energy gap ($\Delta E_{ST}$) of -0.14 kJ mol$^{-1}$ and high biradical character (0.95), indicating the two electrons are nearly fully disjointed. This is among the highest biradical character reported for boron-containing biradicals.

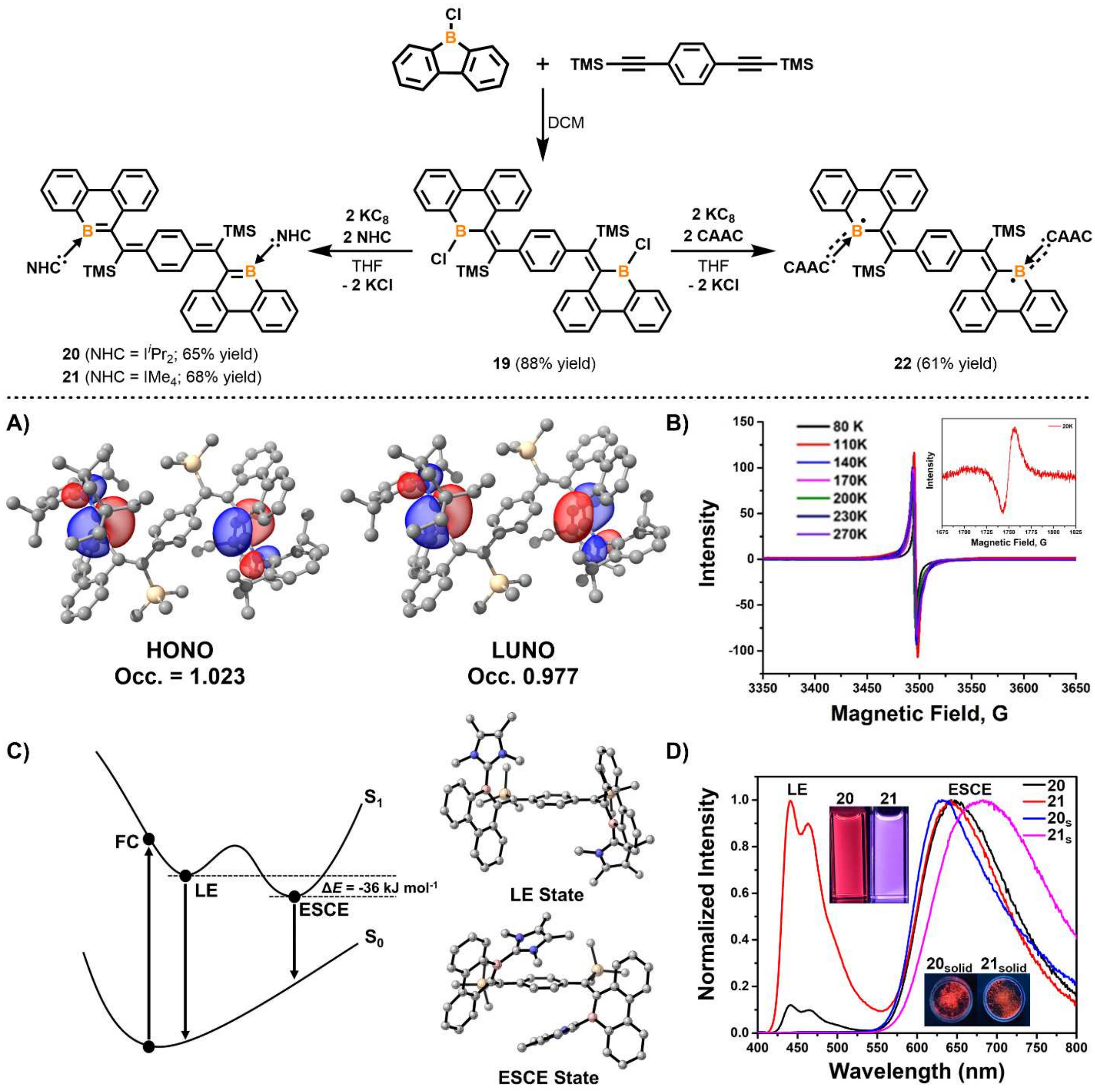


**Figure 2.** Top: Synthesis of neutral bis(9-chloro-9-boraphenanthrene) (**19**) and reduction to closed-shell species (**20**-**21**) and biradical (**22**). Bottom: A) Natural orbitals and natural orbital occupancies of **22**. B) Variable temperature CW X-Band EPR of **22** in THF. Half field transition ($m_s$ = 2) at 20 K shown in inset. C) Potential energy surface of **21**. ESCE dual emission process with optimized geometries. D) Normalized emission spectra of **20** (black) and **21** (red) in THF and

as solids, **$20_{solid}$** (blue) and **$21_{solid}$** (pink); $\lambda_{ex}$ = 350 nm. Adapted with permission from ref 2. Copyright 2023 American Chemical Society.

Remarkably, **20** and **21** showed dual-emission at 441 and 643 nm, with the higher energy band being attributed to the local excited (LE) state and the lower energy band being attributed to an excited state conjugation enhancement (ESCE) process. The notable differences in the LE emission between **20** and **21** may be rationalized by the increased charge transfer character of **21**, a result of increased rotation of the boraphenanthrene moieties when the less sterically demanding $IMe_4$ ligand is employed. Compounds **20** and **21** showed solution quantum yields (QYs) of 6.3% and 3.3% and solid-state QYs of 3.5% and 1.2%, respectively. The increase in QY and bathochromic shift in **$21_{solid}$** compared to **$20_{solid}$** is attributed to the smaller dihedral angle, increasing the conjugation between the NHC and B-heterocycle, which leads to a more prominent ESCE state.

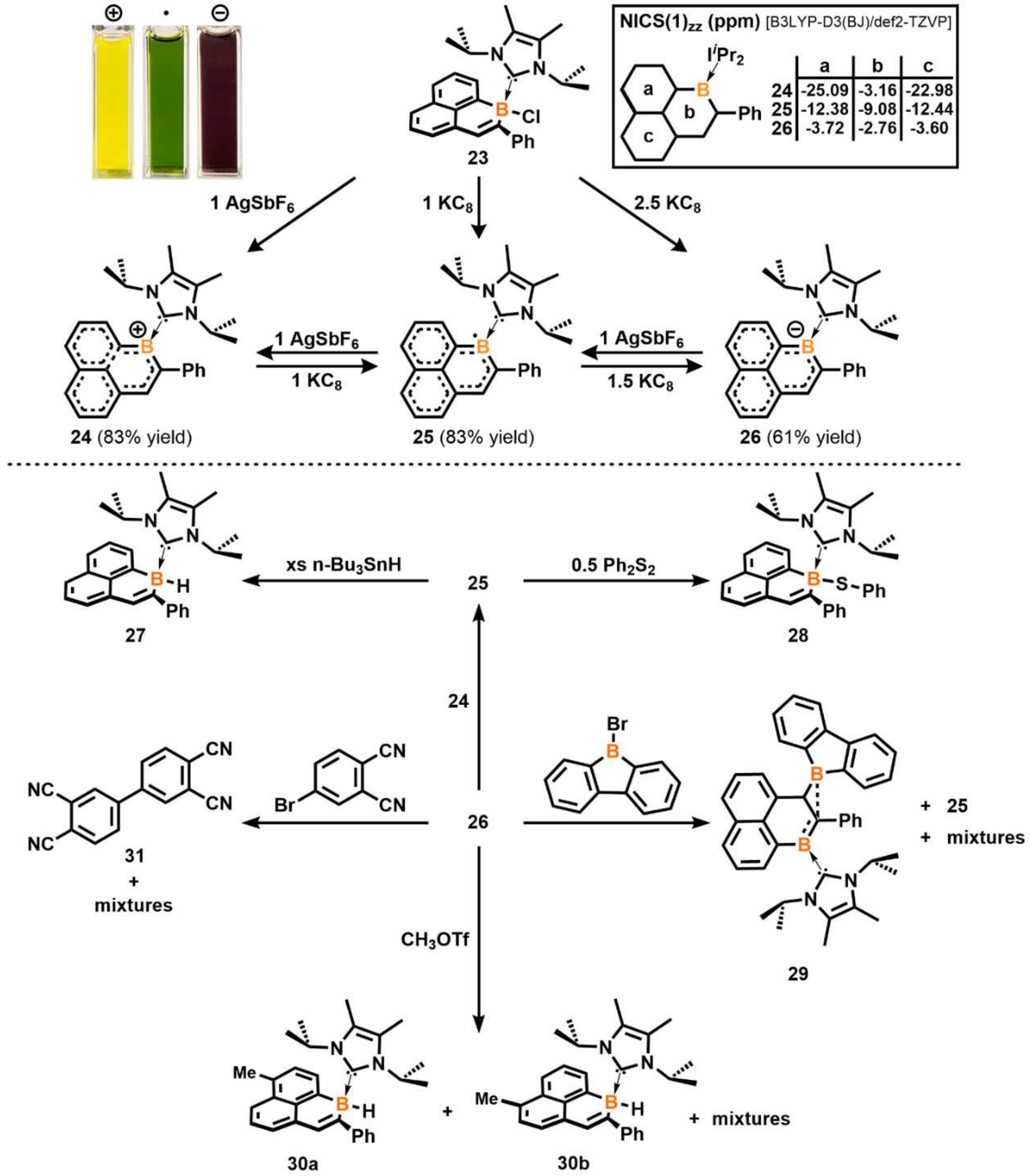
### 3.2 Synthesis of Boraphenalenyl Cation, Radical, and Anion

Phenalenyl, a non-Kekulé hydrocarbon and the smallest triangular fragment of graphene, has attracted interest from materials chemists due to its optoelectronic, spintronic, conductive, and magnetic properties.[31] The ability for the tricyclic molecule to switch between multiple redox states is a key component of understanding the charge transport properties of phenalenyl-based materials. There have been key contributions to the development of neutral boron(III)-containing phenalenes, including the synthesis of B- and BN-phenalenes.[31-32] However, efforts to isolate B-phenalenyl species in different redox states were unsuccessful,[33] and no known B-phenalenyl system possessed the ability to mimic the charge-states of carbonaceous-phenalenyl.

We targeted the Lewis-base stabilized halo-boraphenalenyl using the reported 1-hydroxyl-2-phenyl-1-boraphenalene as a starting material.[32a] Compound **23** was synthesized by chlorinating with $BCl_3$ and subsequently coordinating the $I^iPr_2$-NHC.[4] The NHC-stabilized boracycle undergoes halide abstraction via the addition of $AgSbF_6$ to give the cationic boracycle **24** (Scheme 3). Reduction via the addition of one or two equivalents of $KC_8$ lead to the stable radical (**25**) and anion (**26**), respectively. Compound **25** is among the most stable Lewis base-stabilized B-PAH radicals, surviving in boiling toluene for at least one week. Once isolated, compounds **24**-**26** are stable in the solid-state and can interconvert via the addition of the appropriate equivalencies of $AgSbF_6$ or $KC_8$.

Compounds **23**-**26** were fully characterized by NMR or EPR spectroscopy and X-ray crystallography. The $^{carbene}C$–B bond lengths [1.582(3)-1.594(4) Å] are all very similar, consistent with single bonds, and the additional electrons in the reduced species primarily populate the B-PAH p-orbitals. This is in direct contrast to that observed in reduced borafluorenes in which sequential reduction leads to a more significant shortening of the $^{carbene}C$–B bond due to increased delocalization of the electrons onto the ligand. Also, in contrast to the reduced bis(boraphenanthrene)s **20**-**22**, the boron atom is planar within the 6-membered ring, allowing for more efficient delocalization of the electron density through the triangular fragment. A combination of nucleus-independent chemical shift (NICS) values and anisotropy of the induced current density (ACID) plots for **24**-**26** indicated that all three rings are aromatic. This retention of aromaticity across the three redox states is consistent with the all-carbon analogue but is rare for organoboron species.

**Scheme 3. Top: Synthesis of boraphenalenyl cation (24), radical (25), and anion (26). Bottom: Reactivity of 25 and 26.**



NICS(1)$_{zz}$ (ppm) [B3LYP-D3(BJ)/def2-TZVP]

| | a | b | c |
|---|---|---|---|
| 24 | -25.09 | -3.16 | -22.98 |
| 25 | -12.38 | -9.08 | -12.44 |
| 26 | -3.72 | -2.76 | -3.60 |

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We began our reactivity studies with the radical species **25**, to understand if a radical that is highly delocalized throughout the B-PAH reacts at the boron center, PAH skeleton, or both. Reaction of **25** and a H• source, n-$Bu_3SnH$, resulted in the formation of the boron hydride product **27** as the sole product. Similarly, the reaction of **25** with diphenyldisulfide gave a singular boraphenalenyl sulfide product **28**. Adding excess reagent to **25** in either case did not result in reactivity at any other site on the boraphenalenyl backbone. In notable contrast, reactivity studies performed with **26** resulted in complex mixtures of products. The reaction between **26** and 9-bromo-9-borafluorene resulted in a dark green solution and the crystallization of **29** and **25** from a mixture of unidentified products. The reaction color and crystallization of radical species **25** indicated that the reaction likely proceeded through a SET-type mechanism. Similarly, the reaction with methyl triflate resulted in a mixture of products where **30a** and **30b** were identified. New B–H bonds are formed via H-migration from the PAH and a methyl group adds to two different sites on the boraphenalenyl backbone. Finally, the reaction between **26** and 4-bromo-phthalonitrile resulted in a reductive coupling product **31**, which was isolated and characterized from a mixture by column chromatography. We concluded that the delocalization of electron density in **26** results in multiple nucleophilic sites and thus complex mixtures. Although controlling product selectivity remains difficult at this stage, this type of reactivity is contradictory to other reduced boracycles, which exhibit boron-centered reactivity. Thus, we believe that late-stage (post-reductive) substitution chemistry may soon be a viable strategy for the development of functionalized B-PAHs.

## 4. Reduced 7-Membered Boracycles: Borepins

Borepin, an aromatic 7-membered boron-containing heterocycle, is the boron-doped analogue of the tropylium ion.[34] Because of the unique non-benzenoid aromaticity achieved with borepin, it has garnered attention in organic and materials chemistry as a platform for building novel boron-based PAHs.[35] Since the synthesis of the first borepins in 1960,[36] numerous neutral borepins have been isolated.[35] Our laboratory isolated the first examples of borepin cations (i.e., borepinium ions) in 2019,[17] and they remain exceptionally rare.[37] Due to the propensity of borepins to form non-planar structures, it is difficult to isolate reduced borepin species since the electrons cannot effectively delocalize within the 7-membered ring. Two strategies can be employed to assist in the isolation of these species: 1) increase the steric protection around the electron-rich boron center and 2) utilize a π-accepting ligand to help relieve boron of some electron density.

### 4.1 Synthesis of Monomeric Borepin Radicals and Anions

We first isolated the carbene-stabilized dibenzo[*b,f*]borepin cations[17] and targeted reduced borepins with the same scaffold. While reduction reactions proceed with dibenzo[*b,f*]borepin cations and carbene-supported dibenzo[*b,f*]borepin-halide precursors, the products generated were extremely reactive and prone to decomposition. Therefore, the dibenzo[*b,d*]borepin was used as a starting material for reduction chemistry as the substituent groups sterically protect the boron center. However, due to that increased steric protection, the reaction to form the tetracoordinate CAAC-[*b,d*]borepin did not proceed to completion. Thus, a one-pot reaction with addition of CAAC and $KC_8$ to the dibenzo[*b,d*]borepins was used to yield stable borepin radicals **32** and **33** (Figure 3).[38] In both radicals, the majority of the spin density resides on the ligand [**32** (B1 31%, C1 42%, N1 24%); **33** (B1 30%, C1 44%, N 24%], which contrasts that observed for borafluorene and boraphenalenyl. Cyclic voltammetry of the radicals displayed reversible reduction (**32**: $E_{1/2}$ = -2.12; **33**: $E_{1/2}$ = -2.22) and oxidation waves (**32**: $E_{1/2}$ = -0.74; **33**: $E_{1/2}$ = -0.79) corresponding to the borepin anion and cation. Accordingly, the addition of excess $KC_8$ to **32** and **33** further reduces them to the anionic species **34** and **35**. Compounds **34** and **35** can also be isolated by combining the halo-borepin, carbene, and excess $KC_8$, although the reactions do not proceed as cleanly and purification is a challenge due to the instability of the anionic species.

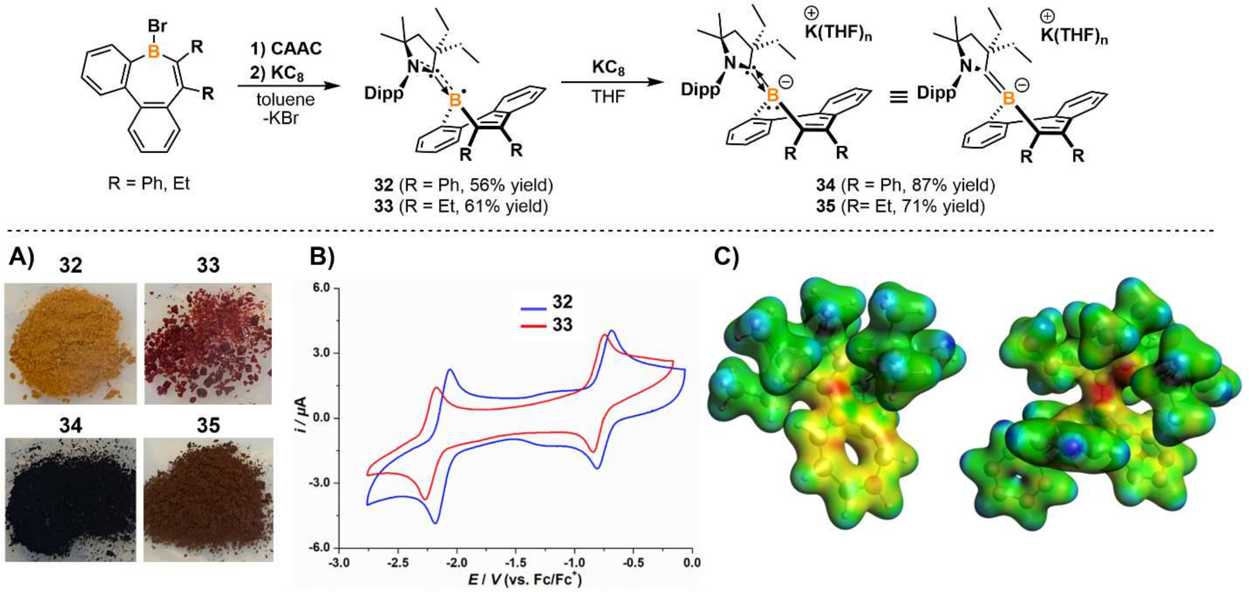


**Figure 3.** Top: Synthesis of monomeric borepin radicals (**32**, **33**) and anions (**34**, **35**). Bottom: A) Pictures of **32**-**35** solids. B) Cyclic voltammograms of **32** and **33** in THF/0.1 M $[nBu_4N][PF_6]$. C) Electrostatic potential maps of the computationally generated unsubstituted borepin anion (left) and **34** (right). Electron density increases from yellow→orange→red. Adapted with permission from ref 38. Available under a CC-BY 4.0 DEED license. Copyright 2022 Hollister, K.K, Yang, W., Mondol, R., Wentz, K.E., Molino, A., Dickie, D.A., Kaur, A., Frenking, G., Pan, S.,* Wilson, D.J.D,* Gilliard, R.J.*

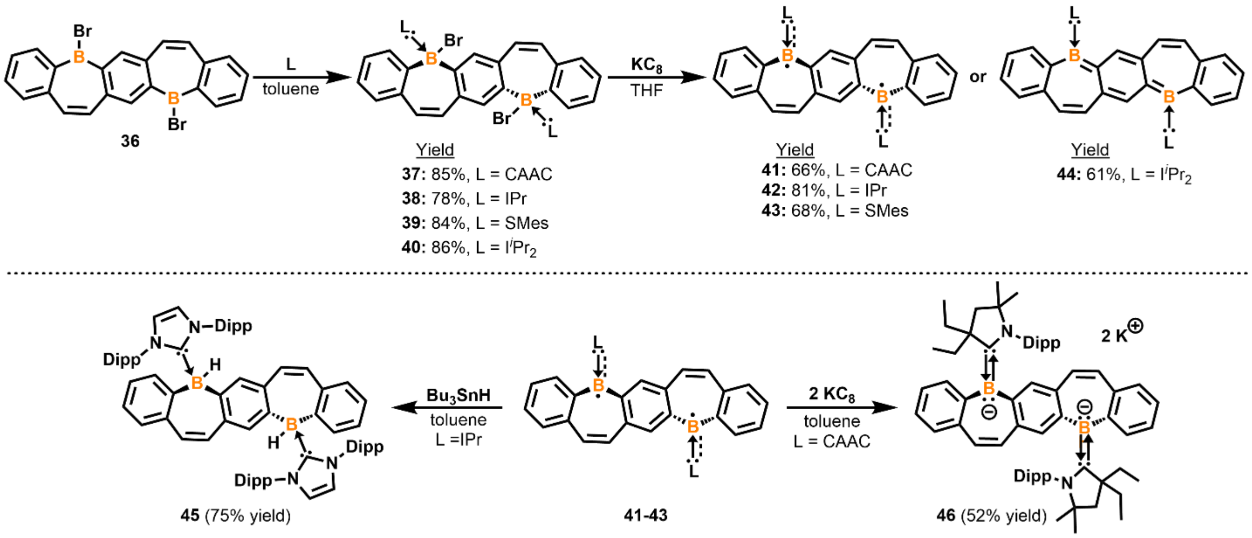
All reduced borepins were structurally characterized and displayed boron centers bent out of the plane of the borepin ring (**32**: 60°; **33**: 55°; **34**: 53°; **35**: 51°), forming a boat-like structure. Theoretical calculations demonstrated that the deviation of the borepin ring from planarity is due to low-frequency vibrations of the annulated rings and substituent groups. The unsubstituted monocyclic borepin anion was theoretically optimized with a planar ring system, and the electrostatic potential map shows alternating electron density distributed through the 7-membered ring (orange regions), consistent with anti-aromaticity. However, due to the non-planar boat-shaped conformation in the substituted borepin anions, the borepin rings are non-aromatic. There is significant negative charge localized to the $^{\mathrm{carbene}}$C–B bond (red region), which supports the lack of efficient electron delocalization to the B-PAH. We also observed a decrease in the $^{\mathrm{carbene}}$C–B bond length as the boron is reduced, further supporting the description of the bonding. Attempts made to isolate the reduced NHC-stabilized borepins through similar reduction strategies were unsuccessful, perhaps unsurprisingly so. With the largely filled p-orbital at the carbene center due to the two adjacent N atoms, the added electron density in the anion is not able to delocalize onto the ligand or bent PAH, resulting in an extremely electron-rich boron center. This is a clear case where the use of CAAC was highly beneficial for the isolation of reactive compounds in cases where diamino-NHCs are insufficient.

## 4.2 Synthesis of Fused Bis-Borepin Biradicals

The realization of reduced borepins allowed us to explore the impact of extending the π-conjugation of the borepin system on their stability and electronics. We sought to employ the neutral ligand approach to the fused bis-borepin scaffold,[39] however, the bis(haloborepin) **36** needed to be isolated. Tin-boron exchange with the reported stannacycle[39] afforded an air- and moisture-sensitive red solid from which single-crystals were grown.[3] Tricoordinate haloborepins are particularly challenging to isolate and prior to the isolation of **36** there was only one structurally characterized example.[34a] They are very Lewis acidic and will even pick up solvent vapors from the glovebox atmosphere, making storage in taped vials in the freezer a necessity.

The Lewis-base adducts were isolated through coordination of **36** with CAAC, IPr, SMes [1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene], or I$^i$Pr$_2$ to give **37-40** (Scheme 4). X-ray crystal structures were obtained of compounds **37-40** which revealed a tetracoordinate geometry at boron with a zig-zag fused borepin (FBP) core. Subsequently, the addition of two equivalents of KC$_8$ to **37-40** in THF afforded the doubly-reduced open-shell borepin biradicals **41-43** or closed-shell diboraquinone-containing diborepin **44**. X-ray structures of **41-43** also gave the zig-zag structure, but **44** was completely planar. In **41-43**, the $^{\text{carbene}}$C–B bonds were slightly shortened [1.525(3)–1.5302(16) Å], suggesting some of the radical electron density resides on the ligand. However, in **44**, the $^{\text{carbene}}$C–B bond length is in the typical range of single bonds and the endocyclic C–B bond is shortened with double bond character. These data revealed a new ligand-based strategy to modulate the core electronic structure of diborepins under steric control. Indeed, the distortion of the FBP core from planarity trended with the increasing steric bulk of the ligand [**41** (64°) > **42** (58°) > **43** (53°) > **44** (4°)]. The bulky N-aryl groups in **41-43** result in a bending of the pentacyclic core and formation of biradicals and the small N-alkyl groups in **44** allow for the planarization of the FBP giving the bora-quinoidal structure (Figure 4).

**Scheme 4. Top: Synthesis of fused bis(haloborepin) 36, tetracoordinate adducts 37-40, and doubly-reduced species 41-44. Bottom: Reactivity of bis-borepin biradicals to form bis(borepin hydride) (46) and bis(borepin anion) (47).**



In **41**-**43**, the solid arrow from the ligand depicts two-electron donation to boron, while the dashed lines represent delocalization of the radical on the ligand. This delocalization is more pronounced in the case of CAAC rather than the NHCs. Adapted with permission from ref 4. Copyright 2024 American Chemical Society.

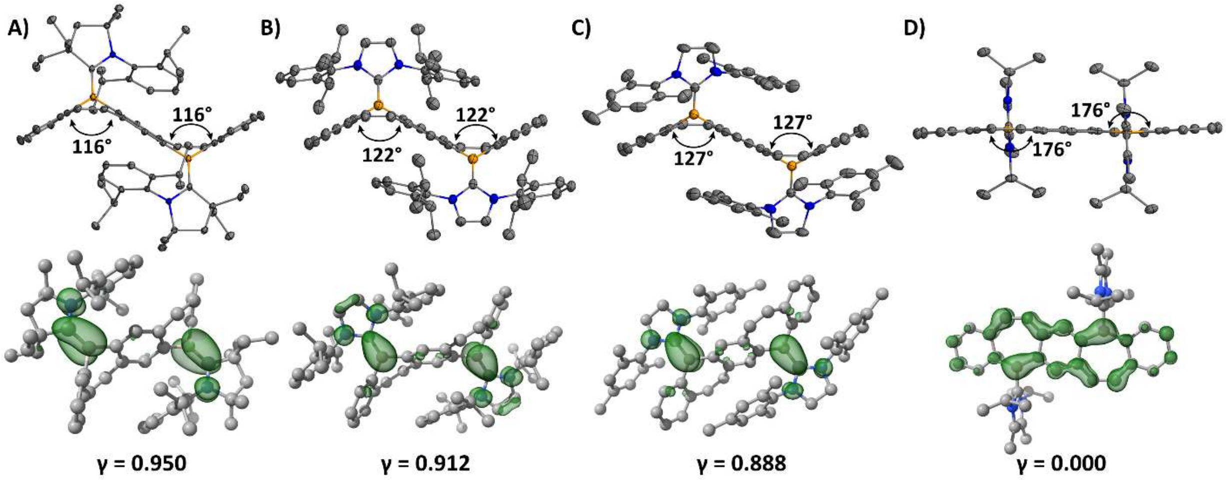


**Figure 4.** Side view of molecular structures with distortion angles (top) and triplet spin density plots (bottom) of **41** (A), **42** (B), **43** (C), and **44** (D). Biradical character (γ) was calculated using complete active space self-consistent field calculations using an active space of two electrons in

two orbitals (CASSCF(2,2)//B3LYP/def2-TZVP). Adapted with permission from ref 4. Copyright 2024 American Chemical Society.

Compounds **41**-**43** showed temperature dependent $m_s = \pm 1$ and $m_s = 2$ EPR transitions. They displayed open-shell singlet ground states with $\Delta E_{ST}$ of -0.451 kJ mol$^{-1}$ (**41**), -0.570 kJ mol$^{-1}$ (**42**), and -0.745 kJ mol$^{-1}$ (**43**), which correlated with the degree of distortion of the FBP core, indicating that the choice of ligand can dictate the percentage of open-shell biradical character (up to 95%). Compound **44** was EPR active at room temperature but had a large calculated singlet-triplet gap ($\Delta E_{\text{CSS-T}}$) of -35.3 kJ mol$^{-1}$, suggesting a thermally accessible triplet state.

In order to probe the open-shell character of our biradicals, we exposed them to $Bu_3SnH$. Biradicals **41-43** reacted to form the bis(borepin hydride), although only the IPr analogue **45** was fully characterized. Efforts to reduce each biradical to the corresponding dianion resulted in the isolation of only the bis(CAAC-stabilized borepin anion) **46**. In the case of the NHCs, either the dihydride was isolated, likely obtained through the reaction with adventitious moisture in solution, activation of the solvent, or shredding of the ligand in the presence of excess reducing agent. Unsurprisingly, due to its π-accepting character, CAAC was able to stabilize the highly electron-rich bis(borepin anion), which was accessed by the addition of two equivalents of $KC_8$ to the biradical **41** or four equivalents of $KC_8$ to the Lewis-base adduct **37**. Consistent with our results on the monomeric borepin system, the NHC-stabilized dianions were not isolable.

## Summary and Outlooks

This Account summarizes our contributions toward the isolation of reduced 5-, 6-, and 7-membered boracycles using a neutral ligand coordination chemistry and reduction strategy. These molecules lead to the formation of boron-element bonds that are synthetically inaccessible by other means and generate new materials with unique reactivity profiles and optical properties. The choice to frequently use $KC_8$ as the reducing reagent stems from the strength of potassium as a reductant and the increased surface area when intercalated into graphite, although many of these reactions proceed with milder one-electron reductants. While similarities exist between the reduction strategies among the different ring systems, these data clearly indicate that ring fusion and size, geometry, and the specific site of boron doping are critical design aspects that influence the properties and functions of reduced B-PAHs. Thus, each system presents new challenges and exciting electronic properties.

The choice of ligand is critical for this type of chemistry as the CAAC-stabilized reduced boracycles were generally easier to isolate and handle, although all compounds are sensitive to air and moisture. Moving from 5- and 6-, to 7-membered rings, we observed an increase in the bending of boron out-of-plane, resulting in more localization of electron density on the boron atoms. In the planar borafluorene and boraphenalenyl systems, the anions could be isolated with NHCs due to the delocalization of π-electrons within the 5- and 6-membered rings. Comparatively, the bending of the borepin system results in unstable NHC-stabilized boracylic anions, leading to decomposition or bond activation. The current trend suggests the NHC-stabilized anions are only stable when the boron ring is planar allowing for delocalization of the electron density within the PAH.

The isolation of borafluorene in three charge-states give rise to distinct electronic structures, properties, and reactivity trends. While studies on the reactivity of borafluorene radicals are underdeveloped, significant progress has been made with borafluorene anions, which display both SET or nucleophilic substitution reactivity in the activation or formation of chemical bonds. Unique boracycles that exhibit fluorescence, capture metal ions, release CO, and form new metal-element bonds have demonstrated the importance of these reduced boracycles for the development of more complex materials. The boraphenalenyl anion has potential regarding the late-stage post-reductive functionalization of reduced B-PAHs as reactivity occurs on the periphery of the phenalenyl skeleton. Future work needs to be conducted to understand how to tune the nucleophilicity at different sites of the boraphenalenyl anion to control selectivity. The reactivity of borepins, 7-membered boracycles, is significantly less understood compared to the 5- and 6-membered ring systems. Our laboratory is currently expanding on the initial borepin reactions that have been discussed and we invite interested researchers to join us in the development of this area. Overall, we hope this Account provides insight into the design strategies associated with isolating reduced boron heterocycles and their potential as molecular building blocks.

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## ABBREVIATIONS

B-PAH, boron-doped polycyclic aromatic hydrocarbon; NHC, N-heterocyclic carbene; CAAC, cyclic(alkyl)(amino) carbene; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; I$^{i}$Pr$_2$, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; IMe$_4$, 1,3,4,5-tetramethylimidazol-2-ylidene; LE, local excited; ESCE, excited state conjugation enhancement; SMes, 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene; FBP, fused borepin

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